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SPECTRAL ANALYSIS OF POWDERS IN WHICH THE POWDERS ARE INTRODUCED INTO THE DISCHARGE ZONE BY MEANS OF AN AIR STREAM

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Spectral analysis is widely used for studying a large number of powdered materials with a heterogeneous composition, such as ores, minerals, slags, oxides, salts, etc..

Unfortunately, the most widely used are methods of quantitative spectral analysis, which are based on evaporation of test material from the canal of the carbon electrodes, do not, by any means, always ensure the requisite reproducibility of results. This is determined to a considerable degree by the fact that during evaporation of test material from the electrode canals, there is inevitably observed a change in the rate at which the elements enter the discharge zone [1], with a consequent change of their concentration in the arc [2]. This is reflected in line intensity and leads to a continuous change in intensity during evaporation. It should be noted that the change in concentration of the elements in the gas cloud, and the subsequent passage of the elements into the arc, often destroy the temperature conditions of arc flame excitation [3, 8, 10], which also affects line intensity.

In a number of cases, change in element concentration in the arc affects the condition of self-absorption and re-absorption of the lines in the arc cloud.

It should be remembered that, apart from normal changes of line intensity with composition of test material, there may be other accidental changes in line intensity. Thus, shifting the arc flame along the surface of the electrodes, and accidental shifts of the arc flame toward the sides, destroy the conditions of entry of the elements into the discharge zone and affect the distribution of the elements in the arc cloud.

Finally, it should be remembered, that shifting the arc flame, in some instances, leads to spectra being photographed in different parts of the gas cloud. From all that has been said above, it follows that the reproducibility of results obtained by arc analysis can only be achieved by ensuring a constant rate of evaporation of the elements, and a constant flow of them into the discharge, and also by stabilizing the position of the flame with respect to the electrodes. These conditions can be attained e. g., by direct introduction of the test material, uniformly, and in small amounts, into the discharge zone, and by reducing the part played by the electrode processes in the evaporation of test material to a minimum. When the discharge temperature is stabilized and when there is complete evaporation of the particles introduced into the discharge, one should expect that the composition of the test will have a smaller effect on line intensity, and consequently, lead to a decrease in systematic errors during analysis of materials with variable composition.

Uniform introduction of small amounts of material can be realized to some extent by pouring the powder through the arc slits [4]. This method of introducing the material into the arc has not however been widely used, since the ascending stream of hot air hinders regular entry of the particles into the flame. Shifting of particles to the side also leads to a large amount of powder falling on the tips of the electrodes and evaporating from the surface of the latter [5].

As our observations showed, regular entry of powdered material into the discharge zone between metallic and graphite electrodes, and satisfactory stabilization of the position of the flame is easily achieved by introducing the

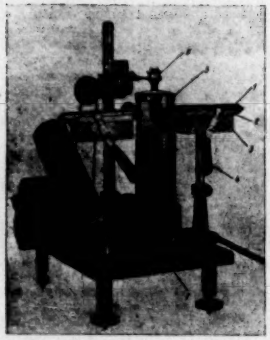

Fig. 1. Apparatus for regular feeding of powders into discharge zones by means of a current of air.

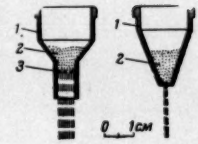

Fig. 2. Funnels for feeding the powder. a) Funnel; 2) powder; 3) sieve.

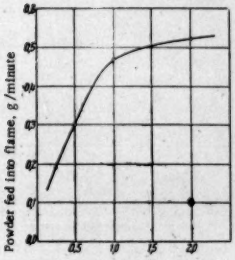

Fig. 3. Relation between the rate at which the powder is sprayed into the flame and the amount of powder in the funnel.

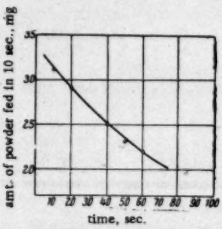

Fig. 4. Relation between spraying rate and duration of spraying.

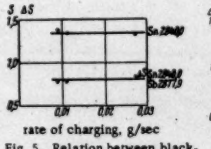

Fig. 5. Relation between blackening of the Sn 2840.0 line and the difference in blackening Δs of the Sn 2840.0 and Sb 2877.9 lines, and the charging rate.

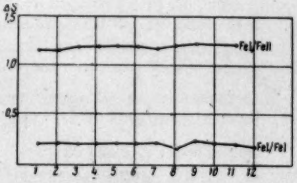

Fig. 6. Changes in the difference in blackening for the lines FeI 3083.7, Fe II 2639.5, FeI 3083.7, and Fe I 2757.3 during charging of ore powder.

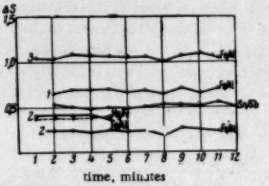

Fig. 7. Changes in difference in blackening of the lines SnI 2840.0 and SbI 2877.9, Fe I 3083.7 and Mg I 2795.5, Fe I 3083.7 and Al I 3082.2 and Fe I 3083.7 and Ni I 3050.8 during charging of powdered ore.

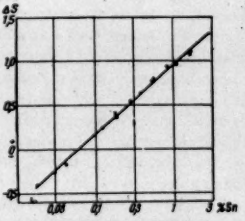

Fig. 8. Relation between difference in blackening of the SnI 2840.0 and SbI 2877.9 lines, and the tin content of the ore.
o – Quartz; + cassiterite (SnO_2);
● – quartz + SnS; x – tin ore;
Δ – cassiterite ore.

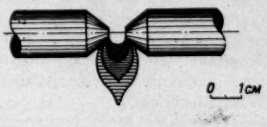

Fig. 9. Position of the arc flame between the copper electrodes.

powder in a very finely ground state into the flame by means of an air stream.

An apparatus constructed with this aim in view can also be used for spark discharge operation.

An Apparatus for Introducing Powders into Arc and Spark Discharge Zones by Means of an Air Stream

The construction of the apparatus for introducing powders into arc and spark discharge zones respectively can easily be followed by examining Fig. 1.

Metallic or graphite electrodes 1 are arranged horizontally on movable massive iron blocks 2, which can slide into the recess of an iron holder 3. The blocks 2 can be brought close to each other or moved away from each other, so that the electrodes can be easily adjusted by means of a hand lever 4. Arc or spark discharges are formed in tube 5, in the top of which openings are made which are covered with asbestos. The electrode ends are introduced into the tube via narrow openings made in the asbestos. The third opening in the tube wall serves as the exit for the light radiated by the discharge. Air is sucked in at a rate of ca. 2 M per second by means of a small chamber in the side of the apparatus fitted with a ventilator. The air throughput in the tube is regulated by rotating a damper in the tube.

0.02-0.5 g of the powder which has been ground so as to pass a 200 mesh sieve is placed in a metal funnel 6 fitted over the tube opening, the outlet of the funnel being covered with a metal sieve. The construction of this funnel, which is designed for giving a wide flow of particles, and also the construction of a funnel for pouring powder in the form of one fine stream, are both shown in Fig. 2.

The funnels most widely used are those with a tube diameter ~ 6 mm, provided with a sieve with openings of 0.2-0.3 mm. The funnel and powder are shaken by means of a five-stage toothed wheel, 10 mm in diameter which is rotated by means of a motor at a rate of 200 revolutions/minute*. During one revolution of the wheel the funnel is lifted 5 times through a height of 1 mm and then, by means of a spring, rapidly returned to its original position, thus giving an impulse to the funnel from below.

When the powder is poured through the funnel fitted with a sieve, a stream of particles is formed which consists of clearly visible individual streams, the number of which corresponds to the number of openings in the sieve (ca. 400 per cm^2).

The air passing along the tube attracts particles of powder, and the latter, without shifting to the side, pass uniformly into the arc flame occupying a stable position with respect to the electrodes. The cone of the arc flame, in contrast to a freely burning arc is formed below. Gaseous products formed during burning of the arc are sucked into the ventilator chamber and are removed through the tube.

The apparatus for supplying the powder need not therefore be under a draft. Powder which accumulates in the tube during operation is removed from the tube through opening 7.

Relation between Line Intensity and the Conditions under which Powder is Fed into the Arc

The air which passes along the tube of the apparatus leads to cooling of the electrodes, and thereby decreases the effect of evaporation processes of the elements in the test material into the arc cloud. This was particularly clearly manifested during work with massive copper electrodes, 12 mm in diameter and 8 cm long.

Thus, a comparison of line intensity for tin in the spectra of tin ores during evaporation of powders in the flame of a copper arc alone, or from the surfaces of the tips of copper electrodes, indicated that the concentration of tin in the gas cloud depends basically on evaporation of particles into the flame. Approximate calculations showed that the concentration of the radiating tin atoms in the arc cloud during evaporation of the powder into the flame is 50-100 times greater than the concentration established during evaporation of the powder from the tips of the electrodes.

In working with copper electrodes therefore, there is no need to fear particles of powder falling on their surface.

Calculation of the concentration ratio N_1/N_2 for these cases of evaporation was carried out by means of the formula

$$\frac{N_1}{N_2} = \frac{I_1}{I_2} \cdot \frac{e^{-\frac{E}{KT_2}}}{e^{-\frac{E}{KT_1}}},$$

* A similar method of producing a rocking action for a small bunker was described recently by Danilova and Sopchik [6].

where I_1 and I_2 - are the line intensities observed; T - the temperature of the arc cloud, and E - the excitation potential of the line.

It must be pointed out that in a number of cases, during forced feeding of particles of easily fusible ores, the latter stick together on the electrode surfaces thereby forming a bridge between electrode tips which prevent normal entry of particles into the flame. Formation of bridges must be avoided and they should be broken up by shifting the electrodes.

Satisfactory results can also be obtained by using rotating copper electrodes [7].

Adjusting conditions for burning the copper arc whereby the particles attracted by the air stream form a wide stream, not only ensures regular feeding of particles into the flame, but also removes danger from changes in the amount of powder fed into the arc, as a result of accidental shifts of the flame to the sides of the electrodes. The downward shift of the arc flame by the air also favors stability, and has a positive advantage from the point of view that the outer "cold" cloud of the flame, in which, at sufficiently high concentrations of the test elements, the effect of self absorption of the lines becomes manifest, is drawn off.

The line intensity in the spectra, other conditions being equal, is determined by the concentration of the element emitting radiation in the gas cloud, and, consequently, depends on the amount of powder passing into the arc in unit time. Nevertheless, an increase in the amount of material sprayed into the arc leads to a comparatively slow increase in line intensity, presumably, as the result of the fact that small particles of powdered ore, under conditions of forced spraying, manage to stick together in the outer zones of the flame to give larger particles which do not evaporate completely in the arc.

Thus, on stepping up the spraying rate of tin and antimony ores three times (from 0.01 to 0.03 g/ second) the line intensity of tin and antimony increases approximately 1.5 - 2 times.

Whether or not satisfactory results are obtained during analysis of ores on the basis of the absolute line intensity of the elements, depends, to a large extent, on the stability of operation of the set-up used for agitating the funnel. It must be pointed out however, that uniform agitation of the funnel cannot guarantee that the powdered ore can be fed into the arc at a constant rate over a period of time, since, as is evident from Fig. 3, the spraying rate depends on the amount of material in the funnel.

A study of the curve given in Fig. 3 shows that an increase in the amount of powder loaded into the funnel, at first leads to a rapid and then a comparatively slow increase in charge velocity. Charging is always accompanied by a decrease in the amount of powder in the funnel, and consequently, its charge rate should gradually drop. An example of such a decrease in charge rate is given in Fig. 4. This relates the amount of powder charged to charging time. 0.25 g of powder was loaded into the funnel, and after every ten seconds, the amount of powder which had been charged into the arc during that time was weighed. A study of Fig. 4 shows that after 60 seconds, the charge rate drops 30 %.

Thus, when carrying out spectral analysis of ores based on measurement of changes in the absolute values of line intensity, it is essential that the charging conditions should be carefully standardized, while the spectra should be photographed not only at a constant exposure time, but account must be taken of the time during which the powder has been fed into the arc before the spectra are photographed.

The introduction of a sufficiently large amount of test material into the funnel decreases the gradual slowing down of the charging rate of the powder, and permits several spectra to be photographed without renewing the material in the funnel. The charge rate of the powder, other conditions being equal, depends on the rate at which the funnel is agitated, and increases with the number of times the funnel is agitated in unit time. In deciding the rate at which the vibrator is to work, one should bear in mind that at slow rates, the ore powders issue from the funnel in separate lots. An activated arc is a discontinuous source of light, in which pauses between spraying of the arc with powder are longer than the burning time of the arc. There is a danger therefore that the particles may happen to pass between the electrodes at the moment when the arc is extinguished. In such cases, changes in the rate at which the motor rotates can affect line intensity and is a possible source of error during spectral analysis of ores. In order to have an idea of the extent of this error when dealing with an activated arc, the duration of time during which the powder is charged into the arc was measured for each agitation of the funnel. A paper disc was fixed on to the axis of a Warren motor and rotated under the funnel from which the stream of particles emerged, at a constant speed. By measuring the areas of the paper which were covered, and uncovered respectively with powder, it was possible to calculate the length of time for which the powder issued from the funnel after each agitation of the funnel, and the time during which no powder was being fed into the arc.

Results of these measurements, carried out at varying rates of funnel agitation are given in Table 1.

TABLE 1

Number of times funnel was agitated per second	Length of time for which powder was actually being fed into the arc after each agitation, in seconds	Interval between charges in seconds
4	0.035	~0.2
9	0.07	~0.06
12 }	Continuous stream	
18 }		

A study of Table 1 shows that the time for which the powder is being charged into the arc zone increases rapidly with increasing agitation rate. When the funnel is shaken more than 12 times a second, the powder passes through the flame in a continuous stream, so that it is possible to use a source of light with any frequency of interruption of the radiated light for exciting the spectra.

In order to check on the reproducibility of the charging of powder into the arc, several chargings were carried out on various samples of tin ores, and the relative error of single charges calculated from the average amount of powder charged.

These results showed that the reproducibility of charging is characterized by a mean arithmetic error of $\pm$ 3%. It should be noted that the charging rate depends to a considerable extent on careful fixing of the funnel in its holder, since, if it is badly fixed, systematic errors may arise which sometimes amount to 30%. It should also be noted that during the charging process, in the case of ores which have been ground to the same degree, the charging rate may change with ore composition, which is reflected in absolute line intensity

As a result, in dealing with ores which differ in charging rate, one should select a sieve such as ensures an approximately equal charging rate into the flame, and that all the powder loaded into the funnel is supplied to the flame.

As an example, we have given in Fig. 5 the blackening values S obtained for the Sn 2840.0 line and the difference in blackening ΔS between the lines Sn 2840.0 and Sb 2877.9, obtained on charging a powdered tin ore at rates of 0.009, 0.011, and 0.027 g/second. 1 g of powder was loaded into the funnel and all of it charged into the arc flame.

In this case, as Fig. 5 shows, not only is there no change in ΔS, but there is none in their blackening either.

Determination of element concentrations by means of the relative intensity of the lines is considered more reliable, since in this case difference in blackening of the lines depends to only a small extent on charging rate.

A copper arc can be considered almost stable in comparison with a carbon arc, in which the appearance of an element, with an ionization potential less than 12 eV gives rise to a decrease in its temperature.

The ionization potential of copper is 7.7 eV, and comparatively few elements with a lower ionization potential decrease its temperature. With respect to this lowering of arc temperature, the most troublesome elements are sodium and potassium which have particularly low ionization potentials (5.1 and 4.3 eV), and which can be present to the extent of a few percent in ores. When such ores are being charged, therefore, it is expedient to add sodium chloride to them in amounts of not less than 10%. When this is done, the differences in blackening of arc and spark lines during replicate photographs of the spectra are sufficiently constant, indicating, therefore, that the temperature conditions of arc excitation are constant.

Fig. 6 shows the differences in blackening of the arc and spark lines of FeI 3083.7 and FeII 2639.5, obtained by taking successive photographs of the ore spectra, as an example. This fig. also contains values of ΔS for the arc lines of iron, 3083.7 and 2757.3, the relative intensity of which should depend to a comparatively small extent on variations in the temperature of the source of excitation of the spectra. In comparing changes in the values of ΔS for the lines FeI and FeII and the lines FeI and FeII of interest is the fact that in both cases the changes are small, and are approximately equal in magnitude.

Measurement of the difference in blackening of lines of different elements, which depends not only on variations in arc temperature, but also on conditions of evaporation of the ore, shows, as is evident from Fig. 7, fairly good reproducibility for ΔS during repeated chargings of various ores. The wave lengths of the pairs of lines examined as well as the differences in their excitation potentials are given in Table 2.

It should be noted that in certain rare cases, during prolonged charging of the ore samples, the particles of the latter under the effect of energetic agitation, can, depending on the shape and size of the grains, their specific gravity and surface properties, be redistributed in the body of the powder. The composition of powder charged into the arc, may thus change with time. Thus, we observed a continuous change in the values of ΔS for lines of tin and antimony during charging of samples of cassiterite ore which had not been ground finely enough, and which contained 1% Sb_2O_3 (internal standard).

TABLE 2

Wave length, in A	Difference in excitation potentials in eV
Tin 2840.0 and antimony 2877.9	0.58
Iron 3083.7 and nickel 3050.8	0.92
Iron 3083.7 and aluminum 3082.2	0.99
Iron 3083.7 and magnesium 2795.5	0.58

Thus, in carrying out ore analysis by this method, one should avoid lengthy charging of the ore into the discharge zone without renewing the amount of material loaded into the funnel, since this may not only lead to regular changes in absolute line intensities, but also sometimes affect the relative intensity of the lines.

Reproducibility of Quantitative Spectral Analysis When the Powder Is Charged into the Discharge Zone with a Current of Air

Determination of the reproducibility of the analytical results obtained by this method was carried out on 150 control analyses of tin ores, using standards similar in composition to the test samples, for constructing a calibration curve.

As an example we have given in Fig. 8 a calibration curve relating difference in blackenings of the lines SnI 2840.0 and SbI 2877.9, and the logarithm of the percentage content of tin in the test. Antimony was added as Sb_2O_3 to all the ores in amounts of 1%. 10% NaCl was also added to the test powders. The powder was introduced into the copper arc flame (10 A, 220 V, Sventitsky activator) in the course of 40 seconds, at the rate of ca. 0.015 g/second. The arc discharge was formed between copper electrodes arranged at a distance of 4mm. The shape of the electrodes and the position of the flame are shown in Fig. 9. A central part of the arc flame, the light from which was directed by means of a three lens illuminator on the slit of a quartz spectrum "ISP-22", was photographed; the photographic plates used were "Spectral, Type I", GOST 2.

The analytical results which are only partly adduced in Table 3, showed that the reproducibility of single determinations of tin in the concentration range 0.003-1% is characterized by a mean arithmetic error of ± 5%; when the spectra are photographed twice, and the tin determined from the mean values of the differences in blackening of the lines, the reproducibility is ± 4%.

Errors connected with photometric measurements of the lines and the non-homogeneity of the plate emulsion were found to be ± 4%.

Thus, of the total errors amounting to ± 5%, the error which can be attributed to non-standard introduction of powders into the flame, and changes in the conditions of radiation of light by the arc is ± 3%. This indicates that the reproducibility of the method can be increased by improvements in the photographic material, or by direct registration of the lines by means of photo-elements.

The reproducibility of analyses based on introducing powders into the discharge zone by means of an air current, usually exceeds by 2-2.5 times that attainable by evaporation of the test from the canals of carbon electrodes. Thus, on using the usually adopted method of evaporation from the canal of a carbon electrode for tin ores, the mean arithmetic error for tin determination when the spectra were photographed twice was found to be ± 9%.

It is known that considerable changes in the composition of test samples, in several cases, destroys the ratio of line intensities, and leads to a shift in the calibration curves, and to the appearance of systematic errors [5,9]. These errors are usually less when powders are introduced into the arc flame than when the test samples are evaporated from the canals of carbon electrode.

An idea of the displacement of calibration curves by both methods of evaporation, for powders of varying composition, can be gained by a study of Figs. 10 and 11.

Quartz powders diluted in a ratio of 1:1 with magnesium oxide, ferric oxide, or calcium carbonate were tested. The powders contained cassiterite (SnO_2) and a constant amount of antimony (1% Sb_2O_3).

Displacement of the curves observed during evaporation of these powders is not a consequence of changes in excitation of the copper arc, since the ratio of the arc and spark lines of the elements remains constant. These displacements are apparently the results of reactions in the outer parts of the flame leading to reaction of SnO_2 and Sb_2O_3 with particles of a "blank nature" and to the formation of new compounds.

At the same time it would be expected that particles of powder would grow because they tend to stick together in the outer parts. A change in the rate at which tin and antimony pass into the flame during incomplete evaporation of enlarged particles of powder with variable composition, during their passage through the flame, may be the reason for the displacement of the calibration curves. No displacement of the calibration curves is observed on switching

TABLE 3

Experiment Number	Composition of test material	Tin in %		Relative error in %
		Taken	Found	
1	Cassiterite ore	0.13	0.13	0
2	" "	0.41	0.41	0
3	" "	0.19	0.18	−5
4	" "	0.060	0.059	−2
5	" "	0.0057	0.0060	+5
6	" "	0.56	0.55	−2
7	Quartz + cassiterite	0.040	0.039	−2
8	" "	0.36	0.36	0
9	" "	0.12	0.14	+16
10	" "	0.12	0.13	+8
11	Quartz + SnS	0.040	0.041	+2
12	" "	0.37	0.36	−3
13	" "	0.030	0.030	0
14	" "	0.17	0.18	+6
15	Quartz-50%, Fe_2O_3-50% + cassiterite	0.020	0.019	−5

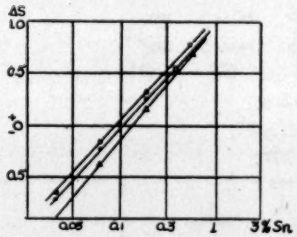

Fig. 10. Relation between difference in blackening of the lines SnI 2840.0 and SbI 2877.9 and the amount of tin in the powders; □ − SiO_2 + SnO_2; O) − SiO_2 − 50%; Fe_2O_3 − 50% + SnO_2; O − SiO_2 − 50%; $CaCO_3$ − 50% + SnO_2; Δ − SiO_2 − 50%; MgO − 50% + SnO_2. Powder introduced into the flame of a copper arc with air.

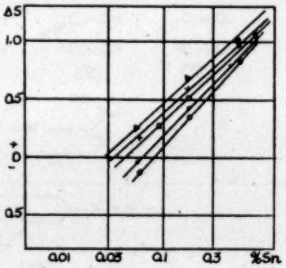

Fig. 11. Relation between difference in blackening of the lines SnI 2840.0 and SbI 2877.9 and the amount of tin in the powders; □ − SiO_2 + SnO_2; O) SiO_2 50%, Fe_2O_3 50% + SnO_2; O − SiO_2 − 50%; $CaCO_3$ − 50% + SnO_2; Δ − SiO_2 − 50%; MgO − 50% + SnO_2; X − SiO_2 − 50%; Al_2O_3 − 50% + SnO_2. Powders evaporated from the canals of carbon electrodes.

from SnO_2 to SnS, both when the powders are introduced into the arc with a current of air, and when they are evaporated from the canal of a carbon electrode.

SUMMARY

1. A method is suggested for charging powders by means of a current of air into the discharge zones of arc and spark discharges. This method increases the reproducibility of spectral analysis.

2. Using tin ores as examples it has been established that the reproducibility of determinations of the elements when the powders are charged with a current of air into a copper electrode, is 2-2.5 times that of the normally adopted method of evaporating ores from the canals of carbon electrodes. It has also been shown that systematic errors which arise during analysis of materials with variable composition decrease on introducing the powders in a copper arc flame by means of a current of air.

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COLOR REACTIONS FOR BERYLLIUM

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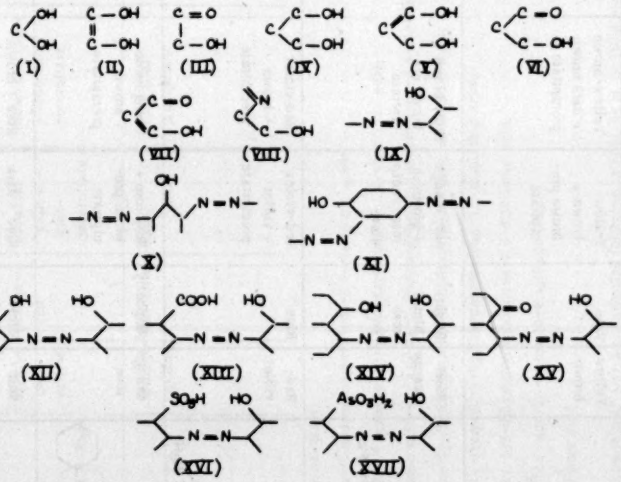
1. New Color Reactions for Beryllium

Since both the sulfide and ammine of beryllium are unstable in the presence of water there is not much point in looking for analytical reagents for beryllium which contain sulfur or amine nitrogen.

Reagents containing the oxygen-containing groups —OH, and =O, are characteristic for beryllium. Since there is no chromophoric activity in the combination Be — O [1], it is essential for color reactions that the chromophoric groups should be contained in the reagent molecule itself, i.e., the reagents themselves should have their own intrinsic color.

During a study of the behavior of beryllium toward a series of reagents containing atomic groups with the following structures

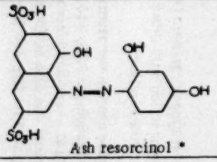
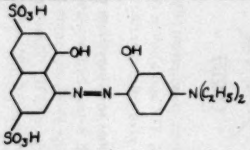
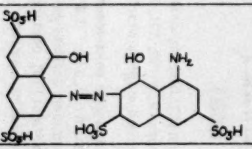
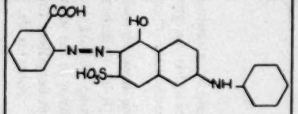
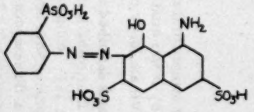


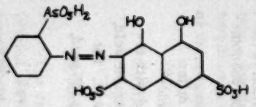
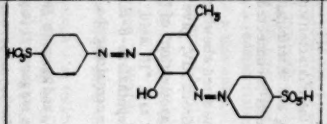
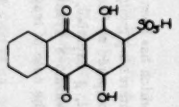
in a similar manner to that used for aluminum [2], lithium, calcium, magnesium [3], antimony, gallium [4], and vanadium [5], it was established that the groups IV, V, VI, VII, X, XIV and also (in conjunction with other groups) III, XIII, and XVII are fairly characteristic of colored reagents which give color reactions with beryllium.

Reagents described in the literature which give color reactions with beryllium also contain the atomic groups listed above. Thus quinalizarin [6-9], naphthazarin [10, 11], 1,4,5,8-tetrahydroxy-anthraquinone [12], and probably, alkanin [10, 11] contain group VI [13]; aluminon contains groups V+VI; curcumin [14] and acetylacetone, which exhibit absorption with beryllium in the ultraviolet [15], contain group VII. These groups can also be found in reagents which give a fluorescence with beryllium in alkaline solutions: morin [16-18], contains (VI + III), and 1-hydroxy-4-aminoanthraquinone [19,20] contains VI.

The mechanism of the reaction of a widely used reagent for beryllium, p-nitrobenzeneazoorcinol [21-24] has not yet been clarified.

Color Reactions of Reagents Used or Detecting Beryllium, when These Reagents are Used with Other Metals, under Conditions where Urotropine or Pyridine is Added to Their Weakly Acid Solutions. Under These Conditions, Mg and Ca do not react (apart from No. 8 and to some extent No. 7).

	Reagent	Overall color of solution + precipitate							
		Reagent alone	Be	Al	Fe^{III}	Ti^{IV}	Zn	Ni	Co
1	 Ash resorcinol *	Yellow-brown	Rose	Yellow-brown + brown precipitate	Yellow-brown + dark brown precipitate	Orangey-brown + light brown precipitate	Rosy brown	Lilac-brown	Brownish gray
2		Rose-orange	Bright bluish rose	Rosy orange + brownish rose precipitate	Rosy brown + brown precipitate	Rose + rose precipitate	Orange-red	Rose	Rose-lilac
3		Red-violet	Blue	Red-violet + violet precipitate	Red-violet + brown precipitate	Reddish blue + white precipitate	Blue-violet	Brown-violet	Olive
4		Orange-rose	Raspberry	Rosy rose + white precipitate	Orange-rose + brown precipitate	Orange-rose + white precipitate	Reddish-rose	Gray-rose	Bright violet
5		Rose	Violet	Rose + dark rose precipitate	Rose + brown precipitate	Rose	Lilac-rose	Red-violet	Brownish lilac

6	 Arsenazo	Rose	Red-violet	Red-violet	Brown lilac	Violet	Rose	Bluish rose	Reddish rose
7		Brownish yellow	Orange-red	Brownish yellow + white precipitate	Brownish yellow + brownish precipitate	Brownish yellow + white precipitate	Brownish yellow	Bluish rose	Brownish red
8		Orange-yellow	Red-violet	Rose	Dirty lilac precipitate	Orange yellow + light precipitate	Rose	Violet	Red-violet

Notes: Standard nomenclature for the reagents:

1) 2,4-Dihydroxybenzene-<1-azo-1>-8-hydroxynaphthalene-3,6-disulfonic acid;

2) 2-Hydroxy-4-diethylaminobenzene-<1-azo-1>-8-hydroxynaphthalene-3,6-disulfonic acid;

3) 8-Hydroxynaphthalene-3,6-disulfonic acid-<1-azo-2>-1-amino-8-hydroxynaphthalene-3,6-disulfonic acid;

4) Benzene-2-carboxylic acid-<1-azo-2>-3-phenylamino-8-hydroxynaphthalene-6-sulfonic acid;

5) Benzene-2-arsonic acid-<1-azo-2>-1-amino-8-hydroxynaphthalene-3,6-disulfonic acid;

6) Benzene-2-arsonic acid-<1-azo-2>-1,8-dihydroxynaphthalene-3,6-disulfonic acid;

7) 1-Hydroxy-4-methylbenzene-2,6-bis[<azo-1>-benzene-4-sulfonic acid];

8) 1,4-Dihydroxyanthraquinone-2-sulfonic acid.

* This reagent under the name "Ash resorcinol" was recommended for boron in 1951 by N. S. Poluektov and M.P. Nikonova. Under the test conditions used for boron, the reagent is insensitive for beryllium [26].

** The synthesis of this reagent has been described previously [27].

Since the reagents described for beryllium, apart from p-nitrobenzeneazoorcinol, contain the same group VI, or groups V and VII which are similar to VI, their properties are fairly similar. All these reagents, e.g., give color reactions with metals which usually accompany beryllium, i.e., aluminum and magnesium; some of their other reactions are also fairly similar.

In the case of beryllium, therefore, when dealing with the reagents listed, it is difficult to increase the practical sensitivity by choosing the most suitable reagent for a given case, as was recommended, e.g., for aluminum [2]. In the presence of reagents containing groups which differ appreciably from each other in their properties, such a possibility is opened up even in the case of beryllium.

New reagents, containing groups XIV, XIII, and XVII, examples of which are given in the table, possess different selective activities than those described in the literature on reagents. Apart from Reagent No. 8, which contains group VI, and which is given for comparison, none of these gives color reactions with magnesium; many of them do not react with aluminum or other elements, either (table).

Nevertheless, as a consequence of other reasons, the new reagents are not always suitable for direct detection and determination of beryllium, or for its detection in the presence of large amounts of other elements. Difficulties arise, since under the conditions employed for carrying out the reactions for beryllium, tri- and quadrivalent cations are precipitated as hydroxides, which adsorb the colored compounds from solution. On the other hand, these new reagents have their advantages.

The fact that reactions are carried out in an almost neutral medium permits masking of several elements with greater success than is possible when using such widely used reagents as p-nitrobenzeneazoorcinol, quinalizarin, and others, in alkaline solutions.

Wenger and Duckert, who carried out a comparative study of reagents for beryllium [25], observed, that in the case of the best reagents, i.e., the best in their opinion, viz., quinalizarin and p-nitrobenzeneazoorcinol, the presence of Mg, Mn, Cu, and Co introduces complications into the detection of beryllium.

These difficulties do not crop up when the new reagents are used. Under the conditions used for detecting beryllium, magnesium does not react with reagents Nos. 1-6 given in the table, and with similar reagents. In alkaline media, reagents Nos. 8 and 7 give bright color reactions with magnesium. When urotropine, which is particularly suitable in the case of reagents Nos. 6, 4, and 5, is used as the neutralizing agent, it is possible to detect beryllium directly even in the presence of 1000 times its amount of manganese.

Copper can be masked with $Na_2S_2O_3$ in neutral media, but not in alkaline media. Using Reagent No. 6 it is possible to detect beryllium in the presence of more than 1000 times its amount of copper, after masking the latter with $Na_2S_2O_3$.

In alkaline media it is impossible to mask elements by means of tartrates, which while not masking beryllium when the latter is pure, exhibit a masking effect when aluminum is also present with the beryllium [6, 7]. In neutral media masking can be carried out with tartrates.

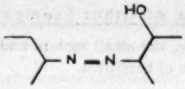
Thus, the possibility of making use of masking techniques, and the changes in the characteristic reactivity of the atomic groups discussed, mean that these new reagents widen the scope for detecting and determining beryllium in the presence of various elements. The mechanism of the color reaction of the new reagents is connected with the phenomenon of intramolecular dissociation of cyclic salts [28].

The sharpness of the color changes, the theoretical basis of which has been considered elsewhere [29], differs from one reagent to the other. Reagents which contain the most interesting group – Group XIV, gave good color changes in all test cases. The reagents which were studied were prepared by "co-diazotization" of "H" acid with resorcinol, resorcinol sulfonic acid, orcinol, diethyl-m-amino phenol, β-naphthol, "R" salt, "H" acid, chromotropic acid, and by co-diazotization of picramic acid in acid medium with 2-amino-8-hydroxynaphthalene-6-sulfonic acid. For the related groups XIII and XVII, a good contrast was observed in the case of reagents containing the residues "I" acid, and phenyl-I-acid (Reagent Number 4).

Of the reagents described, Reagent No. 6 is of interest for qualitative detection, and Reagents Nos. 1, 3 and , , or 4 for the quantitative determination of very small amounts of beryllium. Using these reagents, it is possible to determine beryllium in amounts which are a tenth of those determined by means of p-nitrobenzeneazoorcinol as described

in the literature [22]. At a pH of 5.5, beryllium cannot be found in solution completely as Be^{2+} ions [30]. As a result of the tendency of beryllium hydroxide to form polynuclear hydroxyaquo complexes [31] ("basic salts"), beryllium reacts slowly in dilute solution. It is advisable to heat in order to speed up the reaction.

The reagents described are also of interest for cobalt as well as beryllium. The color reactions of cobalt are related to trivalent cobalt formed by complex formation, on carrying out the reactions, trivalent cobalt, like palladium [32], gives color reactions with the group



Cobalt only reacts in the presence of ammonia or pyridine. Reactions for cobalt will be described in detail elsewhere.

The way in which the new reagents, viz., Nos. 1, 2, 3, 4, 5 or 6, are used for the detection of beryllium in the presence of Mg and Mn, and in the absence of other reacting elements, is completely analogous to that described in the second part of this article for the detection of beryllium in its pure solutions with the reagent arsenazo. The color changes observed are given in the table. With reagents 1, 2, 3, or 6, beryllium gives color reactions at dilutions down to $1:10^8$.

Of particular interest for the colorimetric determination of beryllium, which will be described elsewhere, are reagents 1, 2, 3, and 4. We give below the gist of the method.

Colorimetric Determination of Small Amounts of Beryllium

To 3 ml of a neutral or weakly acid solution containing 0.2-1.2γ Be, are added 0.5 ml of a 0.5-0.1% aqueous solution of reagents Nos. 1, 2, or 3 and 1 ml of 20% pyridine, and the temperature kept at 80-90° for 15 minutes. The color developed is compared with a standard prepared in the same way.

Determination of beryllium is possible in the presence of Al, Fe, the rare-earths, Ca, P, F, and other elements, when these are present in amounts of 50-100 times that of the beryllium.

2. A Color Reaction for Beryllium with Arsenazo.

Among the new reagents for the qualitative detection of beryllium mentioned in the first part of the present article, a useful one is arsenazo (table, No. 6 – benzene-2-arsonic acid- <1-azo-2>-1,7-dihydroxynaphthalene-3,6-disulfonic acid). This reagent, which has been recommended previously for other elements [2, 5, 27, 33] and is of interest also for the colorimetric determination of aluminum, zirconium, hafnium, niobium, and boron, is at present available commercially and is issued by the reagent manufacturing industry.*

Below is given a description of a method whereby beryllium can be detected in the presence of other cations.

BeF_4^{2-} ions do not give the reaction. Phosphates and arsenates complicate the reaction.

Detection of Beryllium in Pure Solutions.

To the neutral or weakly acid test solution are added 1-2 drops of ca. 0.05% aqueous solution of arsenazo, and then a few drops of a 25% urotropine solution, the solution being shaken after addition of each drop of the latter. If beryllium is present, a reddish violet solution is formed; if there is no beryllium, the solution simply acquires the color of the reagent itself - a rose color.

Very dilute solutions of beryllium do not give a color immediately, but only after 1-2 minutes.

Limiting dilution 1:100,000,000.

Limit of detection 0.02γ (in 1 ml at a dilution of 1:50,000,000).

Optimal value of pH ca. 6-6.5.

The drop technique is as follows: a drop of ca. 0.2% solution of the reagent is placed on a filter paper, the paper is dried, and then a micro-drop of the neutral test solution, to which some urotropine has been added beforehand, is allowed to flow out slowly from a capillary tube with a very fine tip (diameter 0.1-0.2mm). If beryllium is present,

* Its synthesis has been described in [27].

then in the center of the white spot formed by "washing" the reagent from the paper, a violet spot will develop, or a point with diffuse edges. At very high dilutions, the spot does not develop at once, but takes about a minute. It is best to let it dry out.

Limiting dilution 1:100,000.

Limit of detection – 0.02γ Be (in 0.002 ml at a dilution of 1:100,000).

Detection of Beryllium in the Presence of Other Elements.

Elements such as magnesium, zinc, manganese, the alkali metals, and others which do not react with arsenazo do not have any appreciable effects on the detection of beryllium.

In addition to beryllium, the following elements give colors when the reaction described above with arsenazo is carried out:

U^{VI} – a blue color [33];

Cu^{II} – a blue-violet color;

Th, V^{IV} – a violet color and precipitate [2, 5, 33];

Fe^{III} – violet, followed by a brown-violet color;

Al, rare-earths, Ga, Sc – red-violet color and precipitate [2, 27];

ZrO^{II}, Pd^{II} – weak bluish-rose color;

Ir^{III} – weak brown-lilac color;

Cr^{III} – (green compounds) – slight darkening;

Ti^{IV} – (larger amounts) – violet precipitate.

Nevertheless, by using suitable complexing agents, all these elements can be masked, after which beryllium can be determined in the presence of any cation.

The various masking agents for the different elements are as follows:

Al, Ga, Fe^{III}, Ti, Zr – tartrates*;

Rare-earths, Fe^{III}, Cu, Ti, Zr – oxalates

Th – tungstates

U – H_2O_2;

Cu – $Na_2S_2O_3$.

Of these complexing agents, $Na_2S_2O_3$, H_2O_2, and tungstates as well have practically no effect on beryllium detection. Ethylene diaminetetracetate (Trilon B) has a weak effect. Tartrates and oxalates, on the other hand, unless carefully used can mask beryllium as well.

Masking of beryllium by tartrates and oxalates, just like masking of any element in general, depends to a large extent on pH. At a pH < 6.5, beryllium is strongly masked, but at a pH of ca. 7, masking of beryllium is so insignificant that for qualitative determination there is no need to worry about it, while under the same conditions masking of aluminum, iron, the rare-earths and others is still effective.

E. g., at a pH of 7, in the presence of one drop of a saturated solution of sodium potassium tartrate per ml of solution, the limiting dilution for beryllium amounts to 1:50,000,000, while in the absence of the tartrate it is 1:100,000,000.

As an example we describe below:

The Detection of Beryllium in the Presence of Aluminum.

To the neutral or weakly acid test solution is added a drop of a saturated sodium potassium tartrate solution per suspected milligram of aluminum (but not more than one drop of tartrate solution per ml of test solution); this is followed

* Sodium ethylenediaminetetracetate which is now available as Trilon B is also suitable.

by a 25% solution of urotropine till the solution is no longer acid to Congo. The solution thus obtained is divided into two. To one part is added a drop of arsenazo solution, while to the other bromothymol blue is added. A saturated solution of borax is then added dropwise to both halves in equal amounts, till the solution containing the bromothymol blue acquires a dark green color corresponding to a pH of 7.

If there is any beryllium in the half containing the arsenazo reagent, the solution will acquire a red-violet color; if no beryllium is present it will remain a rose color.

In order to remove any doubts as to the complete masking of aluminum, the test solution can be divided into three lots, to the third of which is added a small amount of aluminum, e.g., 0.05 mg, and the solution treated as before.

If masking of aluminum is incomplete, then after carrying out this reaction the third part containing the additional aluminum will be colored much brighter than the other to which aluminum was not added. When masking is complete both parts have exactly the same color, corresponding to the amount of beryllium present. In such cases a little reagent is taken.

If the reaction is carried out as described above, it is possible to detect beryllium in the presence of aluminum at ratios of Be: Al = 1:4,000 (3γ Be in 15 ml).

For the detection of beryllium in the presence of iron (Fe^{III}) one can proceed as above, but oxalates are more suitable for masking (Fe^{III}), since the oxalate complex of Fe^{III} has a less characteristic bright color than the tartrate.

Detection of beryllium in presence of up to 500-600 times its amount of iron is possible without complications at higher ratios. However, the yellow color of the Fe^{III} oxalate complex is too bright, and necessitates addition of the same amount of Fe^{III} to the solution used for comparison, or necessitates resorting to use of a comparator.

Using such a technique, 3γ Be can be detected in a volume of 5 – 10 ml for a ratio of Be:Fe = 1 : 1,000 and higher.

5 – 7 drops of a saturated solution of ammonium oxalate are added per milligram of suspected iron.

Fe^{II} at a pH of 7 and higher destroys the reagent.

Rare-Earth Elements, apparently, in general do not complicate beryllium detection. In the presence of oxalates, they simply precipitate, after which the color of beryllium is particularly clearly seen on a white background of the precipitate which has separated out. It is possible to detect quite definitely, e.g., 0.7γ Be in 5 ml of solution at ratios of Be: Σ Rare-earths of 1 : 8,000 and higher.

2 drops of a saturated solution of ammonium oxalate are required per 1 - 1.5 mg $(rare\text{-}earth)_2O_3$.

When oxalates and tartrates are present simultaneously, the rare-earth oxalates may not be precipitated. This does not introduce complications; there is no need to keep the rare-earths in solution.

Uranium is satisfactorily masked by hydrogen peroxide. It forms only a weak, characteristic yellow color when this is done. This color is not very marked even at uranium concentrations of 0.1 mg/ml, so that it is possible to determine beryllium freely in the presence of uranium at ratios up to Be:U = 1 : 200.

At higher ratios it is necessary to use a reference standard containing the same amount of uranium as the test solution. Using such a method, it is possible, e.g., to determine 3γ Be in 5 ml at a ratio of Be:U of 1 : 1000 and higher. The H_2O_2 should be neutral.

Copper at concentrations up to 0.1 mg/ml can be masked with oxalates. On using a reference standard to which copper has been added to give the same bluish color of Cu-oxalate as in the test solution, it is possible, e.g., to determine 3γ Be in 3 ml of solution at a ratio of Be : Cu = 1 : 300.

Larger amounts of copper are masked satisfactorily by $Na_2S_2O_3$. By the use of the latter it is possible to detect beryllium at a ratio of Be Cu = 1 : 1,000 and higher. Copper can also be readily removed by shaking with metallic zinc.

When it is necessary to detect beryllium in minerals, it is sometimes convenient to separate part of the elements which react with arsenazo beforehand, by coprecipitating them with stannic acid which is precipitated on hydrolyzing stannic chloride. Using this technique, the following elements are coprecipitated: Fe, Zr, Ti, Th. Detection of beryllium in the presence of large amounts of aluminum, rare-earths, and copper remaining in solution has already been discussed in the examples given above.

Detection of Beryllium in Minerals.

1. A grain (2-5 mg) of the mineral is carefully ground in an agate mortar, fused on the loop of a platinum wire with sodium carbonate, and the bead formed dissolved in dilute hydrochloric acid; the solution is evaporated almost to dryness and the residue diluted with 5-10 ml of water.

2. 1-2 drops of a 60% aqueous solution of $SnCl_4$* is added and the solution taken to the boil, and, if the solution has a strong acid reaction toward Congo, $NaHCO_3$ is added dropwise till the solution gives only a weakly acid (the solution must not be neutralized!) reaction (violet color of Congo paper); the solution is then boiled and filtered.

3. A saturated solution of sodium potassium tartrate and ammonium oxalate are then added to the filtrate, followed by a 25% solution of urotropine, till the solution is no longer acid to ongo.

Two equal volumes of solution are then transferred to two test tubes. To one is added 1-2 drops of 0.05% solution of arsenazo, while bromothymolblue is added to the other. An equal number of drops of a saturated solution of borax is then added to each test tube, until the test tube containing the bromothymol blue acquires a dark green color.

If beryllium is present, the solution containing the reagent acquires a red-violet color, which does not change on addition of H_2O_2 (control reaction).

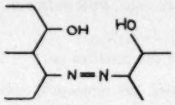
Note. In the absence of large amounts of phosphate, arsenate iron, and thorium section 2 above can be omitted. The presence of thorium can be detected by the development of a violet color with the reagent in acid solution [33]. In neutral media, thorium can be masked by adding sodium tungstate.

One grain of beryl gives a very definite reaction for beryllium.

The reactions described above were worked out in 1946; publication has been held till 1955.

SUMMARY

Atomic groups are listed whose presence in the molecules of colored organic reagents leads these reagents to give color reactions with beryllium. Examples are given of new reagents which give sensitive, and contrasting color reactions with beryllium. Of particular interest are reagents which contain a group with the structure



and by means of which it is possible to determine 0.2 – 1 γ of beryllium colorimetrically, and detect it at dilutions up to 1 10^8.

The reagent arsenazo – [benzene-2-arsonic acid-<1-azo-2> – 1,8-dihydroxynaphthalene-3,6-disulfonic acid] forms a red violet color with beryllium in neutral solution, whereby beryllium can be determined at dilutions down to 1 : 100,000,000. Limit of identification 0.02 γ Be.

All other elements which react under these conditions can be masked: Al – by tartrates or Trilon B, Fe^{III}, the rare-earths, and Cu-by oxalates, U – by hydrogen peroxide; and Th – by tungstates, after which beryllium can be detected in the presence of : 4,000 times its amount of Al, > 1000 times its amount of Fe, U, and Cu, and > 8000 times its amount of rare-earths.

A method is described for detecting beryllium in minerals.

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* The commercial product which does not fume in air, and is called "stannic chloride", is a ~ 60% aqueous solution of $SnCl_4$. Pure $SnCl_4$ fumes strongly in damp air.

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VOLUMETRIC DETERMINATION OF BERYLLIUM

HYDROLYSIS OF BERYLLIUM SULFATE BY MEANS OF A KI - KIO_3 MIXTURE

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A new volumetric method is described for determining beryllium which is based on hydrolysis of an aqueous solution of beryllium sulfate by means of KI - KIO_3, in the presence of excess sodium thiosulfate, and titration of excess thiosulfate with standard iodine solution. Another possible use of the iodide-iodate mixture is also suggested.

Hydrolysis of solutions of metal salts with a mixture of KI - KIO_3 is well known in quantitative inorganic analysis [1-3]. Thus, the hydroxides of iron, aluminum, chromium, and uranium are precipitated quantitatively with simultaneous evolution of iodine when neutral or weakly acid solutions of their salts are treated with excess of iodide-iodate mixture. In the present work, beryllium is determined either gravimetrically by calcining the hydroxide to give the oxide, or by titrating the iodine which is liberated with standard thiosulfate. Preliminary tests carried out in these laboratories show that an aqueous solution of beryllium sulfate is hydrolyzed in the same way as the other metals mentioned above, if it is treated with KI-KIO_3 mixture. Since very little information has been published re this reaction, it was thought desirable to examine the hydrolysis reaction mentioned, and its possible application to the volumetric determination of beryllium systematically. This work is described in the present article.

EXPERIMENTAL

Aqueous solutions of beryllium sulfate were prepared by dissolving the requisite amounts of a pure Merck sample of the sulfate. The beryllium was determined by the classical method [4].

To an aliquot of $BeSO_4$ solution, contained in a 250 ml Erlenmeyer flask fitted with a glass stopper, was added excess 0.05 M KIO_3 3-5 g KI and a measured excess of standard thiosulfate. The flask was then stored for 4-5 hours in a thermostat at 50-60 °. After cooling, excess thiosulfate was titrated with standard iodine.

The amount of iodine liberated during hydrolysis was calculated from the inital and final titers, and from this the amount of beryllium in the test solution, by means of the equations:

$$3BeSO_4 + KIO_3 + 5KI + 3H_2O \rightarrow 3Be(OH)_2 + 3K_2SO_4 + 3I_2, \quad (1)$$

$$5Na_2S_2O_3 + 3I_2 \rightarrow 3Na_2S_4O_6 + 6NaI. \quad (2)$$

Thus, $BeSO_4 + I_2 = 2Na_2S_2O_3$ or 1 ml of 1N thiosulfate of iodine corresponds to 0.01251 g BeO.

Several tests were carried out, in which, after total hydrolysis of $BeSO_4$ as described above, the precipitated $Be(OH)_2$ was filtered off on a Whatman No. 42 paper, washed with water till it was completely free of excess iodide, calcined, and then weighed as BeO. Table 1 contains the results of volumetric and gravimetric determinations.

DISCUSSION OF RESULTS

Beryllium sulfate is hydrolyzed in water to a considerable extent according to the following equation [5, 6]:

$$BeSO_4 + 2H_2O \rightleftharpoons Be(OH)_2 + H_2SO_4. \quad (3)$$

The sulfuric acid thus formed liberates iodine from the mixture of iodide and iodate

$$IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O \quad (4)$$

and thus favors reaction (3). Nevertheless, under these conditions it was observed that only 84-86% $BeSO_4$ is hydrolyzed (See Table 2).

We know from published results that reactions which occur with incomplete liberation of iodine from KI-KIO_3 give quantitative results if the system initially contains an excess of sodium thiosulfate [7, 8]. Addition of

TABLE 1

Volume of $BeSO_4$, in ml	Strength of the iodine solution, in N	Volume of I_2 in ml = $Na_2S_2O_3$			BeO by the NH_4OH method, in g, x	BeO calculated in g		Difference	
		Added	Unreacted	Reacted		From weight a	By means of iodine b	x − a	x − b
10	0.05318	29.00	22.85	6.15	0.004097	–	0.004091	–	0.000006
20	0.05318	29.00	16.75	12.25	0.008194	–	0.008147	–	0.000047
25	0.05318	29.00	13.60	15.40	0.010243	0.01018	0.01024	0.000063	0.000003
30	0.05318	29.00	11.50	18.50	0.01226	–	0.01230	–	0.00004
10	0.05718	26.60	7.65	18.95	0.01350	0.01340	0.01355	0.00010	0.00005
20	0.05336	28.90	8.55	20.35	0.01360	–	0.01358	–	0.00002
40	0.05318	36.25	11.60	24.65	0.01638	–	0.01640	–	0.00002
25	0.05336	36.12	10.60	25.52	0.017025	–	0.01703	–	0.000005
50	0.05318	36.25	5.55	30.70	0.02048	0.02036	0.02042	0.00012	0.00006
30	0.05336	36.12	6.05	30.07	0.02043	–	0.02006	–	0.00037
25	0.05696	67.00	20.20	46.80	0.03350	0.03328	0.03334	0.00022	0.00016

TABLE 2

Thiosulfate normality, N	Volume of thiosulfate = I_2 liberated, in ml	Weight of BeO by the NH_4OH method, in g	BeO, calculated in g		% Hydrolysis		Duration of heating at 50-60°
			From Weight a	By means of thiosulfate b	a	b	
0.07123	24.40	0.03010	–	0.02174	–	72.22	15 minutes
0.1087	17.70	0.02825	–	0.02407	–	85.13	1 hours
0.07123	28.50	0.02920	–	0.02539	–	86.93	$2\frac{1}{2}$ hours
0.07123	29.00	0.02920	0.02520	0.02534	86.30	88.45	4 hours
0.07713	26.90	0.02920	–	0.02596	–	88.90	5 hours

thiosulfate, according to Kolthoff [8] lowers the iodine concentration to a minimum and this favors a rapid reaction even at low H^+ concentrations. The hydrolysis of $BeSO_4$ with $KI-KIO_3$ was therefore studied in the presence of sodium thiosulfate. It was established that this hydrolysis gives accurate and reproducible results if it is carried out at 50-60° in the course of 4-5 hours, over a fairly wide beryllium concentration range. Since under these conditions it was necessary to check on the stability of the sodium thiosulfate solution, preliminary tests were carried out, the results of which are included in Table 3. These results show that sodium thiosulfate is stable for several hours at 50-60°. Since the standard methods for determining beryllium are, for the most part, gravimetric, and necessitate tested experimental conditions, it is worth emphasizing the importance of the present titrimetric method.

TABLE 3

Volume of thiosulfate taken, in ml	Volume of 0.05696 N iodine required, in ml	Duration of heating at 50-60°
20	26.75	Preliminary titration at room temperature
20	26.75	1 hour
20	26.75	$2\frac{1}{2}$ hours
20	26.80	4 hours
20	26.75	6 hours

At present work is being carried out on the use of $KI-KIO_3$ for the volumetric determination of vanadium.

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DERIVATIVES OF TRIHYDROXYFLUORONE AS REAGENTS FOR TIN AND ANTIMONY

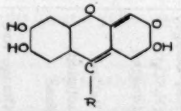
V. A. Nazarenko and N. V. Lebedeva

Derivatives of 2,3,7-trihydroxy-6-fluorone have been used as reagents for antimony (9-methyltrihydroxyfluorone [1, 2 3]), germanium (9-phenyltrihydroxyfluorone [4]), molybdenum and copper (9-hydroxyphenyltrihydroxyfluorone [5]). 9-Phenyltrihydroxyfluorone (phenylfluorone), has been used for the colorimetric determination of germanium [6], and molybdenum [7].

The reaction with trihydroxyfluorone derivatives has in each individual case been described as specific. Nevertheless, a careful study of these and other 9-substituted trihydroxyfluorones shows that a fairly large number of elements react with them. All the same, thanks to their high sensitivity, reactions with trihydroxyfluorone derivatives can be used for qualitative and quantitative analysis in conjunction with suitable techniques of masking and separation.

Tin and antimony are among those elements which react with 9-substituted trihydroxyfluorones. The reactions of tin and antimony with these compounds are of considerable importance since they permit these two metals to be detected and colorimetrically determined with a high degree of sensitivity.

The table contains the results of tests on derivatives of 2,3,7-trihydroxy-6-fluorone, substituted in position 9, and with the general formula



as reagents for tin and antimony, where R-is phenyl, hydroxyphenyl, nitrophenyl, and other radicals. All these compounds were synthesized from triacetylhydroxyquinone and the respective aldehydes—benzaldehyde, salicylaldehyde, nitrobenzaldehyde, etc.[1, 8]. The reagents were tested in 0.05% solution, for the preparation of which 50 mg of the respective compounds were dissolved with gentle heating in 100 ml of 96° alcohol and 1 ml 6N hydrochloric acid.

Antimony reacts with fluorones in the trivalent state, while tin reacts with them in the quadrivalent state. Antimony (V), and tin (II), do not react. The reagents were tested in sulfuric and hydrochloric acid solutions respectively, at concentrations ranging from 0.1 to 6N. For the reactions with tin, the solution also contains 5% sodium chloride. In the absence of sodium chloride, the sensitivity of the reaction for tin is very low, presumably as a result of hydrolysis and formation of colloidal solutions of metastannic acid. Increasing the sodium chloride concentration above 5% leads to a decrease in sensitivity, thereby indicating that tin does not react with fluorones in the form of $SnCl_6^{2-}$ ions.

The reaction was carried out by adding 0.5 ml of reagent to 5 ml of tin or antimony solution, containing not more than 10γ of the element and a definite amount of acid.

As a rule, with increasing acidity, the reaction sensitivity fell, and at 5 – 6 N no reaction was observed.

Tin and antimony form colored precipitates with fluorones. At low concentrations of the element, there is only a change in color as a result of the formation of a stable, colloidal suspension of the colored precipitate. Colloidal solutions of the fluorone compounds of tin and antimony are readily stabilized by gelatin, so that it is possible to use these reactions for colorimetric determinations.

Tin, as can be seen from the table, does not react with compounds I, IX, XII, and XV, under the test conditions. Formation of colored precipitates with these compounds is only observed at high tin concentrations. The most interesting reagents, by means of which it is possible to detect down to 0.5γ of tin in 5 ml of solution, are the compounds III,

Compound number	R	Control	Tin		Antimony	
			Color of precipitate	Sensitivity	Color of precipitate	Sensitivity
I	Methyl	Brown-yellow	Brown-yellow solution	–	Dirty rose	–
II	Phenyl	Yellow	Orange	1 : $2.5 \cdot 10^6$ (0.1N HCl or H_2SO_4)	Orange-rose	1 : $5\ 10^6$ (1N HCl or H_2SO_4)
III	2-hydroxyphenyl	Yellow	Orange	1 : $5 \cdot 10^6$ (0.1N HCl) 1 : $1 \cdot 10^7$ (0.1N H_2SO_4)	Red-Orange	1 : $1 \cdot 10^7$ (0.1N HCl) 1 : $2.5 \cdot 10^7$ (0.1N H_2SO_4)
IV	4-hydroxyphenyl	Light yellow	Yellow-orange	1 : $1 \cdot 10^6$ (0.1N HCl or H_2SO_4)	Orange	1 : $1 \cdot 10^7$ (0.1N HCl or H_2SO_4)
V	4-methoxyphenyl	Yellow	Orange	1 : $1 \cdot 10^6$ (0.1N HCl or 0.5N H_2SO_4)	Red-orange	1 : $2.5 \cdot 10^7$ (0.1N HCl) 1 : $1 \cdot 10^7$ (0.5N H_2SO_4)
VI	4-hydroxy-3-methoxyphenyl	Yellow	Orange	1 : $5 \cdot 10^6$ (0.1N H_2SO_4)	Orange-rose	1 : $1 \cdot 10^7$ (0.1N HCl or H_2SO_4)
VII	2-hydroxy-1-naphthyl	Lemon-yellow	Orange (HCl) Rosy-orange (H_2SO_4)	1 : $1 \cdot 10^6$ (0.1N HCl) 1 : $1 \cdot 10^7$ (0.1N H_2SO_4)	Orange-rose	1 : $1 \cdot 10^7$ (0.1N HCl or H_2SO_4)
VIII	2-nitrophenyl	Yellow	Orange	1 : $5 \cdot 10^6$ (0.1N HCl or H_2SO_4)	Red-orange	1 : $5 \cdot 10^7$ (0.3N HCl or 0.1N H_2SO_4)
IX	3-nitrophenyl	Yellow	Yellow solution	–	Red-orange	1 : $2.5 \cdot 10^6$ (0.1N HCl) 1 : $1 \cdot 10^7$ (0.1N H_2SO_4)
X	4-nitrophenyl	Yellow	Rose	1 : $1 \cdot 10^7$ (0.1N HCl or H_2SO_4)	Raspberry-red	1 : $1.7 \cdot 10^7$ (0.1N HCl) 1 : $2.5 \cdot 10^7$ (0.1N H_2SO_4)
XI	2,4-dinitrophenyl	Yellow	Orange-rose	1 : $5 \cdot 10^6$ (0.1N HCl) 1 : $1 \cdot 10^7$ (0.1N H_2SO_4)	Orange-red	1 : $1 \cdot 10^7$ (0.1N HCl) 1 : $2.5 \cdot 10^7$ (0.1N H_2SO_4)
XII	2-hydroxy-3-nitrophenyl	Yellow	Yellow solution	–	Rose solution	–
XIII	2-hydroxy-5-nitrophenyl	Yellow	Orange	1 : $5 \cdot 10^6$ (0.1N HCl) 1 : $1.7 \cdot 10^6$ (0.1N H_2SO_4)	Red-orange	1 : $1 \cdot 10^7$ (0.1N HCl or H_2SO_4)
XIV	4-hydroxy-3-methoxy-6-nitrophenyl	Yellow	Orange-rose	1 : $5 \cdot 10^6$ (0.1N HCl or 0.3N H_2SO_4)	Orange-red	1 : $1 \cdot 10^7$ (0.3N HCl or H_2SO_4)
XV	4-Dimethyl-aminophenyl	Yellow	Yellow solution	–	Orange-red	1 : $2 \cdot 10^7$ (0.1N HCl or H_2SO_4)
XVI	2-Methoxy-3,4-methylenedihydroxy-2-ethyl-β-methylaminophenyl	Lemon-yellow	Orange	1 : $1.7 \cdot 10^6$ (0.1N H_2SO_4)	Red-orange	1 : $2.5 \cdot 10^7$ (0.1N H_2SO_4) 1 : $1 \cdot 10^7$ (0.1N HCl)

VI, VII, VIII, X, XI, and XIV; of these, compound III (salicylfluorone) is particularly suitable for nephelometric determination of tin, while compound X (p-nitrophenylfluorone) is ideal for colorimetric determinations.

Antimony reacts with all the test compounds. The most sensitive reagents for the qualitative detection of antimony are compounds II, III, IV, V, VIII, X, XIV, and XVI, which can be used also for the colorimetric determination of this element.

Below we give a brief description of the colorimetric determination of tin with p-nitrophenylfluorone (X), and of antimony with phenylfluorone (II).

Determination of Tin. To 10 ml of test solution containing 5% sodium chloride, and which is 0.1 N with respect to sulfuric or hydrochloric acid, is added 0.5 ml of 1% gelatin solution; the whole is mixed, and 0.5 ml (for 0.5 – 10γ Sn) or 1 ml (for 10 – 30γ Sn), of a 0.05% solution of p-nitrophenylfluorone added. The whole is mixed again, and after 45 minutes the extinction is measured, using a green filter (530 mμ) in a 10 – 20 mm cell, and as blank a similar solution not containing tin. The tin content is determined by means of a calibration curve. The relation between extinction and tin content within the limits 0.5 – 30γ Sn is linear under the conditions indicated.

Tin may be separated from other elements by distilling it as the tetrabromide from a mixture of sulfuric and phosphoric acids. Traces of free bromine which may get into the distillate can be removed with phenol as tribromophenol. If antimony is present as well, it is oxidized by the bromine to the quinquevalent state, excess bromine being removed with phenol.

Determination of Antimony. To 10 ml of test solution, which is 1.0 N with respect to sulfuric acid, is added 1 ml of a gelatin solution, the mixture is shaken up, and then 0.5 ml of a 0.05% solution of phenylfluorone added and the whole mixed again. After 30 minutes, extinction is measured using a green filter (530 mμ), in a 5 – 20 mm cell against a similar solution free of antimony. The antimony content is determined from a calibration curve. Beer's law holds under the conditions within the limits 0.5 – 20γ Sb.

Antimony may be separated from other elements which react with fluorones by extracting with ether as the pyridine iodide complex from 8 N sulfuric acid containing 5% tartaric acid. The ether extract is shaken with 1.0 N sulfuric acid, when the antimony goes into the aqueous phase, which can then be used for colorimetric determination with phenylfluorone.

SUMMARY

1. Derivatives of 2,3,7-trihydroxy-6-fluorone, substituted in position 9, are highly sensitive reagents for tin (IV), and antimony (III), and are suitable for the detection and colorimetric determination of these elements.

2. 9-(4'-Nitrophenyl)-2,3,7-trihydroxy-6-fluorone (p-nitrophenylfluorone) permits determination of microgram amounts of tin. Phenylfluorone is used for the determination of similar amounts of antimony.

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FLUORESCENT DETECTION OF THALLIUM AND MERCURY

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The hydrated Tl^+ ion is known to be a carrier of luminescent properties [1, 2], both in solution and in solid materials – phosphors on an alkali halide base.

The Hg_2^{2+} ion also has the properties of forming luminescent compounds. This is apparently related to the fact that the atom of mercury has the same electronic shell and spectral scheme of terms as the Tl^+ ion, i.e., it can be a center of luminescence of equal value to thallium [3].

This similarity in the luminescent properties of univalent mercury (or, more accurately, of the atom of mercury, since the Hg_2^{2+} ions can be regarded as an ion of divalent mercury, activated by mercury, Hg^{2+}, Hg) and thallium is the starting-off point of the present work.

Detection of Thallium

Qualitative detection of thallium chemically has up to the present required a long process of separation and concentration of the thallium. Spectral detection of thallium is also bound up with preliminary enrichment.

We used the property mentioned above, of the hydrated Tl^+ ion to photoluminesce on introducing it into the lattice of an alkali halide, for its detection. As a result of tests which we carried out, it was established that on adding Tl^+ ions to a solution of an alkali halide, and evaporating, the crystals formed photoluminesce on irradiation with ultraviolet light.

We tested the chlorides, bromides, and iodides of the alkali metals as well as ammonium carbonate. They all fluoresce on adding Tl^+ ions. The most intense photoluminesence is produced on adding Tl^+ ions to a solution of ammonium iodide, as can be seen from Table 1. The drop in intensity of the luminescence of films containing thallium can be arranged in the following series:

$$NH_4I > NH_4Cl \gg KI > KCl > KBr \gg (NH_4)_2CO_3 \gg \text{pure } Tl_2SO_4$$

The property of Tl^+ ions to penetrate into the lattice of ammonium and potassium iodides during crystallization, which we discovered, confirms the existence of a diagonal relationship between thallium and the subsidiary sub-group in the first group of the Mendeleev periodic system (univalent copper, silver, and gold). All the elements of this sub-group, like thallium, form luminescing crystals with ammonium iodide. Nevertheless, by observing certain conditions, it is possible to detect thallium even in the presence of these metals (with the exception of copper) which fluoresce similarly.

Crystals of $NH_4I \cdot Tl$, prepared by simple crystallization, obey the same laws of excitation of photoluminescence as those which are known for aqueous solutions and films of alkaline-halides activated by thallium, and obtained by distillation in a vacuum, distillation in air, or by grinding [4].

It is clear from Table 2 that the color of the luminescence of the reaction products of ammonium iodide and Tl^+ ions depends on Tl^+ ion concentration, i.e., there is a redistribution of the intensity maxima in the luminescence spectra: on increasing the thallium concentration, the photoluminescence maximum is shifted to the longer wave-length part of the spectrum. This may serve as a means of getting a relative evaluation of thallium concentration in a test sample. At thallium concentrations ranging from that of a saturated solution to 1.2 mg/ml, an intense luminescence is observed on excitation both with short and long wave-length ultraviolet light.

It should be noted that the color of the luminescence of a dried-out spot is not uniform. During the drying process, crystallization starts at the edges of the drop, where interaction between thallium and ammonium iodide is most intense. Nevertheless, since the drop tends to contract, most of the material crystallizes in the center of the drop

TABLE 1

Characteristics of Luminescent Films Containing Thallium

Composition	Aggregate state	Color of the luminescence	Brightness	Concentration in the drop 0.001 ml
Tl_2SO_4	Solution	Does not luminesce	–	196 μg Tl^+
Tl_2SO_4	Solid	Yellow-green	Weak	0.1 μg Tl^+
Tl_2SO_4	"	Blue	Very weak	0.01 μg Tl^+
$Tl^+ + (NH_4)_2CO_3$	"	Yellow-green	Average	1.2 μg Tl^+; 24 μg $(NH_4)_2CO_3$
$Tl^+ + (NH_4)_2CO_3$	"	Green	Weak	0.1 μg Tl^+; 24 μg $(NH_4)_2CO_3$
$Tl^+ + (NH_4)_2CO_3$	"	Greenish	Very weak	0.01 μg Tl^+; 24 μg $(NH_4)_2CO_3$
$Tl^+ + NH_4I$	"	Yellow	Very bright	1.2 μg Tl^+; 72.5 μg NH_4I
$Tl^+ + NH_4I$	"	Blue	Bright	0.01 μg Tl^+; 72.5 μg NH_4I
$Tl^+ + NH_4Cl$	"	Yellow	Average	1.2 μg Tl^+; 26.5 μg NH_4Cl
$Tl^+ + NH_4Cl$	"	Weak yellow	Weak	0.1 μg Tl^+; 26.5 μg NH_4Cl
$Tl^+ + KCl$	"	Yellow-green	Average	0.1 μg Tl^+; 37 μg; KCl
$Tl^+ + KBr$	"	Yellow	"	0.1 μg Tl^+; 59 μg KBr
$Tl^+ + KI$	"	Green	"	0.1 μg Tl^+; 83 μg KI

TABLE 2

Relation between Luminescence of NH_4I : Tl and Thallium Concentration

Concentration of Tl^+ ion in mg/ml	Color of luminescence at λ 365mμ	Color of luminescence on excitation with λ 313 mμ	Intensity
19.67	Yellow	Yellow	Bright
1.24	Yellow-green	Yellow-green	"
0.12	–	Blue	"
0.012	–	Turquoise green	Average
0.0012	–	Violet blue	"

Therefore, at average thallium concentrations, luminescence is determined by illumination of the center of the spot obtained. The periphery of the spot exhibits luminescence which corresponds to a lower thallium concentration. At very low concentrations, all the thallium is precipitated on the periphery.

A study of the effect of elements which accompany thallium on the course of the reaction used for detecting thallium, in particular, the effect of oxidizing agents, showed that practically no element except copper interferes with thallium detection. The luminescence is partially extinguished when Fe^{3+} ions are present in solution, as a result of liberation of iodine, which absorbs the ultraviolet. It was shown that Fe^{2+} ions do not extinguish the luminescence. It is necessary, therefore, to reduce Fe^{3+} to Fe^{2+} with stannous chloride, or to complex it with phosphate or fluoride ions; fluorides give the best results.

Analytical Procedure. A drop of test solution is placed on an object plate of quartz or normal glass *. A drop of 0.5 N ammonium iodide is added to the first drop, mixed, and then evaporated at a moderate temperature so that crystallization rate is slow. After complete evaporation, the spot is examined in the dark field of an ultraviolet microscope. If thallium is present, a yellow or turquoise blue photoluminescence is observed.

Limit of indentification 0.00012 μg of thallium ions at a limiting concentration of 1:10,000,000. Limiting ratio of thallium to accompanying cations is as follows:

$Tl^+ : Cd^{2+} = 1 : 1{,}000{,}000$ for 0.012 μg Tl^+ ions
$Tl^+ : Zn^{2+} = 1 : 10{,}000$ " 0.012 μg Tl^+ "
$Tl^+ : Ni^{2+} = 1 : 10{,}000$ " 0.012 μg Tl^+ "

* In this case the glass is placed on the object stage of a microscope on the front face, with the reaction product on the side of the excitation source.

Detection of Mercury

We used the property of the halides of univalent mercury to fluoresce on irradiating with ultraviolet, for detecting mercury. A characteristic of mercury halides is the capacity to photoluminesce without first penetrating into the lattice of a basic substance, alkali-halides. E.g., calomel, Hg_2Cl_2, on excitation with the near-ultraviolet (λ365 mμ) photoluminesces with an orange-red color. Pringsheim and Fogel [5], reckon that calomel only fluoresces when it is absolutely chemically pure. If the calomel contains $HgCl_2$ and free mercury, apart from any other contaminants, then, according to these authors, there will be no fluorescence. Nevertheless, our experiments did not confirm this. We observed fluorescence in calomel obtained by reduction of mercuric chloride. We shall describe below how we managed to get calomel which fluoresced from mercuric chloride. Our experiments showed that no fluorescence is observed in calomel if there is free nitrogen peroxide in the solution of the mercuric salt used for the preparation of the calomel. If commercial analytical grade mercuric nitrate is dissolved in water and nitric acid used to get it into solution, and then this solution used for preparing calomel, the product obtained does not fluoresce. If the mercuric nitrate is recrystallized before use, then in all cases, the calomel formed fluoresces brightly with an orange-red color. On mixing a solution of mercuric nitrate with solutions of chlorides, sulfates, and nitrates of ammonia, potassium, sodium, magnesium, barium, calcium, strontium, iron, aluminum, zinc, manganese, chromium, cobalt, nickel, copper, mercury (II), bismuth, lead, silver, tin, cadmium, and antimony we always observed fluorescence of the calomel. Fluorescence of calomel, on excitation with long wave ultraviolet, arises because of the activation of the compound by mercury atoms. The Hg_2^{2+} ion, can, as already pointed out, be regarded as $Hg^{2+} \cdot Hg$, i.e., activation of mercuric chloride by mercury $HgCl_2 \cdot Hg$. This permits formation of calomel to be used for the identification of mercury in a mixture. In addition to fluorescence in calomel, we also observed fluorescence in mercuric bromide Hg_2Br_2 and mercury borate (I).

a) Detection of Mercury by means of Calomel Fluorescence

Analytical Procedure. A drop of test solution is placed on a quartz object glass. A drop of concentrated hydrochloric acid is placed alongside it. After mixing, the precipitate formed is examined in the dark field of the microscope. If mercury is present a bright orange-red fluorescence is observed.

If trivalent iron is present in the test solution, it is essential to wash the precipitate with concentrated hydrochloric acid.

The limit of identification is 0.005 μg of mercury ions at a limiting concentration of 1:200,200. The limiting ratios of mercury to accompanying elements at which the reaction can be carried out without a preliminary separation of these elements, are:

$Hg_2^{2+}:Cu^{2+}$ = 1:2,000 for 0.1 μg Hg_2^{2+} ions
$Hg_2^{2+}:Bi^{3+}$ = 1:2,100 " 0.1 μg Hg_2^{2+} "
$Hg_2^{2+}:Pb^{2}$ = 1:1,600 " 0.1 μg Hg_2^{2+} "
$Hg_2^{2+}:Ag^{+}$ = 1:40 " 0.1 μg Hg_2^{2+} "
$Hg_2^{2+}:Sn^{2+}$ = 1:2,600 " 0.1 μg Hg_2^{2+} "
$Hg_2^{2+}:Sb^{3+}$ = 1:700 " 0.1 μg Hg_2^{2+} "

Divalent mercury is detected in the same way. In this case, however, a drop of stannous chloride is placed alongside the test drop instead of hydrochloric acid. After reduction the precipitate is washed with concentrated hydrochloric acid, and the fluorescence examined in the dark field of the microscope. It is better still to use ascorbic acid as the reducing agent, since in this instance we avoid possible reduction to metallic mercury.

Formation of calomel can also be used for detecting mercury, using its property of absorbing the ultraviolet. The procedure is similar. On examination under the microscope a fluorescent converter is used, and a "UFS-1" light filter placed in the path of the ultraviolet. In the presence of mercury the precipitate is red.

Limit of identification. 0.006 μg mercury ions at a limiting concentration of 1:167,000. The limiting ratios to other cations are as follows:

$Hg_2^{2+}:Cu^{2+}$ = 1:1,500 for 0.1 μg Hg_2^{2+} ions
$Hg_2^{2+}:Bi^{3+}$ = 1:1,500 " 0.1 μg Hg_2^{2+} "
$Hg_2^{2+}:Pb^{2+}$ = 1:300 " 0.1 μg Hg_2^{2+} "
$Hg_2^{2+}:Ag^{+}$ = 1:40 " 0.1 μg Hg_2^{2+} "
$Hg_2^{2+}:Sn^{2+}$ = 1:1,700 " 0.1 μg Hg_2^{2+} "
$Hg_2^{2+}:Sb^{3+}$ = 1:400 " 0.1 μg Hg_2^{2+} "

b) Detection of Mercury from the Fluorescence of Hg_2Br_2.

On mixing solutions of mercury salts (I) and potassium bromide, a precipitate of mercurous bromide is formed which fluoresces brightly with a red-orange light.

Analytical Procedure. A drop of test solution is dried out on a quartz object plate and covered with a drop of a 5% solution of potassium bromide. If mercury is present, on examining the spot in the dark field of a microscope, a bright orange-red fluorescence is observed.

Limit of Identification. 0.004 μg of mercury ions at a limiting concentration of 1:250,000. The limiting ratio of mercury to accompanying cations is as follows:

$Hg_2^{2+}:Ag^+ = 1:100$ for 0.1 μg Hg_2^{2+} ions
$Hg_2^{2+}:Pb^{2+} = 1:1,200$ " 0.1 μg Hg_2^{2+} "
$Hg_2^{2+}:Bi^{3+} = 1:400$ " 0.1 μg Hg_2^{2+} "

In the presence of a large amount of soluble salts of other elements the precipitate is washed 2-3 times with a solution of potassium bromide.

This reaction can be used for detecting mercury on the basis of absorption of the ultraviolet. The analytical procedure is the same. Bismuth goes into solution as $K_3(BiBr_6)$; the precipitate will contain lead in the form of needle-like crystals of lead bromide which absorb in the ultraviolet, while the mercury will be in the form of a flocculent precipitate which is red under the microscope. No other ions interfere in practice.

The limit of identification is equal to 0.005 μg of mercury ions at a limiting concentration of 1:200,000. The limiting ratio of mercury to accompanying cations are as follows:

$Hg_2^{2+}:Ag^+ = 1:90$ for 0.1 μg Hg_2^{2+} ions
$Hg_2^{2+}:Pb^{2+} = 1:900$ " 0.1 μg Hg_2^{2+} "
$Hg_2^{2+}:Bi^{3+} = 1:300$ " 0.1 μg Hg_2^{2+} "

c) Detection of Mercury from the Fluorescence of the Borate.

Mercury borate (I) exhibits a bright green fluorescence. Mercury (I) can be detected by means of it. The formation of mercury borate can only be used to a limited extent, since bismuth, lead, and iron salts extinguish the fluorescence of the borate at ratios as low as 1:1.

Analytical Procedure. To a drop of test solution on a quartz object glass is added a few grains of borax, which are then mixed in with a glass rod. If mercury is present, a bright green fluorescence is observed if the precipitate is examined in the dark field of the microscope.

The limit of identification is 0.4 μg of mercury ions at a limiting concentration of 1:7,500.

If iron, bismuth, and lead are absent, the given reaction can be used for detection of mercury on the basis of absorption of the ultraviolet. The procedure adopted is the same as before. All the reactions described were carried out on a Brumberg [6] ultraviolet microscope. When it was necessary to examine reaction products under the microscope in the light of the fluorescence, the fluorescent converter was removed from the field of vision of the microscope, and a "UFS-1" light filter placed in the path of the ultraviolet; this filter passes light from 400 to 250 mμ. Another filter which can be used is the "UFS-3" which transmits the near ultraviolet (λ 365 mμ).

N. N. Grigorev participated in the first half of the work.

SUMMARY

1. A fluorescent reaction for detection of thallium, based on the formation of $NH_4I \cdot Tl$ is described.

2. Reactions are described for the detection of mercury by means of the fluorescence of the chloride, bromide, and borate of univalent mercury.

3. The possibility has been demonstrated of using these reactions for detecting mercury, on the basis of absorption of the ultraviolet.

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CHEMICO-ANALYTICAL PROPERTIES OF XANTHATES

III. COLORIMETRIC DETERMINATION OF COBALT AS THE ETHYLXANTHATE COMPLEX

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Ethylxanthate complexes are soluble in non-aqueous solvents ($CHCl_3$, CCl_4, C_6H_6, etc.), according to published results [1-4].

The present article contains the results of tests on a qualitative study of the relation between the extractability of ethylxanthates by a few organic solvents, (C_6H_6, CCl_4, $CHCl_3$, CH_2ClCH_2Cl, gasoline) and the pH of the aqueous phase. In addition, a colorimetric method has been developed for determining cobalt as the ethylxanthate complex in the presence of iron, nickel, and other cations.

Extraction of Ethylxanthate Complexes by Non-aqueous Solvents

Analytical Procedure. A solution of the metal salt plus potassium ethylxanthate was placed in a separating funnel. An insoluble ethylxanthate complex of the metal was thereby formed. 5 ml of the organic solvent was then added, after which the pH of the solution was adjusted to a definite value (indicator paper) by addition of hydrochloric acid (1:9), or ammonia (1:6). The contents of the flask were shaken, the non-aqueous layer removed and filtered through a dry filter. The filtrate was evaporated to dryness; the dry residue worked up with concentrated nitric acid, and the respective cations detected.

Results of these tests are given in Table 1.

TABLE 1

Experiment No.	Cation	Color of the solid ethylxanthate complex	Carbon tetrachloride *			Color of extract
			pH ~4	pH ~7	pH ~9	
1	Ni^{2+}	Brownish yellow	e	e	p. e.	Yellow-green
2	Cu^{2+}	Yellow	f	f	f	–
3	Co^{2+}	Dark green	e	e	e	Dark green
4	Mo^{V}, Mo^{VI}	Violet-red	e	d	d	Violet-red
5	Bi^{3+}	Bright yellow	e	p. e.	d	Yellow
6	Pb^{2+}	Pale yellow	p. e.	f	d	Pale yellow
7	Sn^{2+}	Yellow	e	d	d	Yellow
8	Cd^{2+}	White	f	f	f	–
9	Ag^{+}	Light yellow	f	f	f	–
10	Fe^{3+}	Brown	e	e	d	Brown
11	Zn^{2+}	White	e	p. e.	d	Colorless
12	Hg^{2+}	Light yellow	p. e.	f	f	–
13	As^{III}	White	p. e.	d	d	Colorless
14	Sb^{III}	Pale yellow	p. e.	d	d	Pale yellow
15	V^{V}	Bright yellow	e	d	d	Yellow
16	Cr^{VI}	Green	p. e	d	d	Green

Legends: e-extracted; p. e.-partially extracted; f-floats; d-destroyed.

It is clear from this table that the following cations form xanthate complexes which are insoluble in water: Zn^{2+}, Fe^{3+}, Ni^{2+}, V^{V}, Co^{2+}, Sn^{2+}, Sb^{III}, Sn^{IV}, Bi^{3+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}, Hg^{2+}, Cu^{2+} and Ag^{+}. The xanthate complexes

* The ethylxanthates have a similar solubility in other solvents ($CHCl_3$, dichloroethane, benzene, gasoline).

of copper, silver, cadmium, mercury, and uranyl are not extracted by non-aqueous solvents, while the complexes of the other cations enumerated above are extracted by non-aqueous solvents, the percentage extraction falling with increasing pH of the aqueous phase. In alkaline media, only cobalt xanthate is extracted; all the remaining xanthate complexes either decompose, or are not extracted in alkaline media. The tungstate ion is reduced by ethylxanthate to form tungsten blue, which is not extracted. Cations of the alkali and alkaline-earth metals are not precipitated, and do not form intensely colored compounds with xanthate. Ions of aluminum, scandium, yttrium, the rare-earths, titanium, zirconium, hafnium, thorium, and manganese do not react with xanthate.

Mention is made in the literature [3], that chromium reacts with xanthate only when it is in the sexivalent form. We did not manage to find any indications re the composition of the reaction product. Experiments show that xanthate reacts not only with Cr^{VI} but also with Cr^{2+}, and, on long standing, even with Cr^{III}. If excess xanthates are introduced, the end product is obviously the same in each case. We did not succeed in establishing the composition of the reaction products. Nevertheless, the light absorption curves of solutions of the reaction products in CCl_4 are of a practically uniform shape in all cases. A solution of the final reaction products in CCl_4 has a blue-violet color.

Thus, it can be assumed that Cr^{VI}, Cr^{III}, and Cr^{2+} form xanthate complexes. The slow reaction between Cr^{III} and a xanthate can obviously be explained by the fact that trivalent chromium is found as the stable aquo-acid complexes [5], in solution.

Solutions of their xanthates in non-aqueous solvents can be used for the colorimetric determination of nickel, cobalt, and molybdenum [6]. Although the ethylxanthate complex of chromium is intensely colored, its formation is slow and is not quantitative. Trivalent iron is partially reduced by xanthates to the divalent state, which does not react with xanthates, so that this reaction cannot be used for the colorimetric determination of iron. Non-aqueous solutions of the remaining ethylxanthate complexes are only weakly colored and are of no interest for colorimetry. In such cases, extraction of the ethylxanthates can be used for separating cations, or for the extraction of one cation from several other cations in order to concentrate it for analytical purposes.

Colorimetric Determination of Cobalt

Preliminary Experiments. A method was described long ago [2], for separation of nickel and cobalt by treating their xanthates with ammonia. Preobrazhensky [7], however, did not get satisfactory results on checking this method. Our experiments showed that on treating the mixed precipitate of the ethylxanthates of nickel and cobalt with excess ammonia, nickel ethylxanthate goes into solution. Nevertheless the cobalt ethylxanthate precipitate contains a considerable amount of nickel. High results are therefore obtained for cobalt. If cobalt ethylxanthate is precipitated in ammoniacal media, the results obtained are far too low. This can be explained, obviously, by the fact that cobalt in ammoniacal media, is oxidized by atmospheric oxygen to the trivalent state, and the latter, as is known, forms a stable ammine:

$$K_{Co(NH_3)_6^{3+}} = 2.2 \cdot 10^{-34}. \quad [8] .$$

Completely different results are obtained if all these operations are carried out with solutions of nickel and cobalt ethylxanthates in non-aqueous solvents. When ammonia is allowed to act upon non-aqueous solutions of nickel and cobalt ethylxanthates, the first goes completely into the aqueous phase, while the cobalt ethylxanthate remains in the organic solvent phase. If the aqueous ammoniacal solution of nickel and cobalt is allowed to react with potassium ethylxanthate, and the cobalt ethylxanthate then extracted with a non-aqueous solvent, the cobalt cannot be separated from nickel, obviously, because of the reasons advanced above.

A Study of the Composition of Cobalt Ethylxanthate

There are divergent views in the literature about the composition of cobalt ethylxanthate. Some authors [3] say that it is the xanthate of divalent cobalt that is formed; according to others [2, 9] it is the xanthate of trivalent cobalt which is formed.

A decision re the valency of cobalt on the basis of an analysis of precipitated cobalt xanthate is difficult, since the product which separates out contains dixanthates and free sulfur as contaminants. To determine the composition of cobalt ethylxanthate, therefore, we used Ostromyslensky's method [10].

Gekht [4], also studied the composition of cobalt ethylxanthate by this method. According to his results, the composition of the complex corresponds to the xanthate of trivalent cobalt. Judging by his thesis, I. I. Gekht only studied the extreme points of the isomolar mixtures, and then having drawn a straight line through these points,

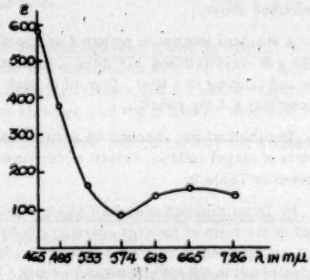

Fig. 1

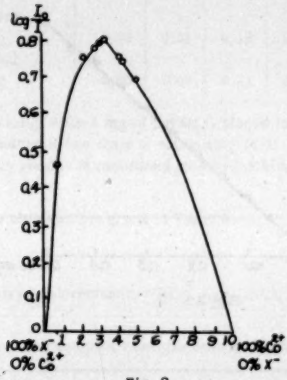

Fig. 2

decided on the composition of the complex. We feel however, that in this case one cannot draw conclusions on the basis of an extrapolation of the experimental data, since the cobalt xanthate complex, although it is stable, is one of the components of a mixture (potassium xanthate being the other), which readily decomposes in acid media. It was essential therefore to get more experimental points near the maximum of the curve composition-light absorption, and not to extrapolate. The experimental points near the maximum of the composition-light absorption curve show that the composition of the complex corresponds to a ratio of 1:2.

Experimental Technique. 0.1 M solutions of cobalt sulfate and potassium ethylxanthate were made. These solutions were mixed in a separating funnel in various proportions, so that the total volume was a constant. 5 ml of the organic solvent was then added, followed by 1 ml of HCl (1:9), and the contents of the funnel shaken. When the layers had separated, the non-aqueous phase was run off, and the color intensity of this phase measured on an FM photometer. Light absorption curves of solutions of cobalt ethylxanthate in CCl_4 which are shown in Fig. 1, were taken in order to select the appropriate light filter. Wave-length is plotted in mμ along the abscissa (Fig. 1), while optical density, expressed as the molar extinction coefficient is plotted along the ordinate.

On the basis of the results given in Fig. 1, all further measurements were made at 465 mμ.

Results of the study of the composition of cobalt ethylxanthate are given in Fig. 2. It is clear from this diagram that the composition of cobalt ethylxanthate corresponds to a ratio of Co:X = 1:2, where X^- is the ion of ethylxanthate.

Determination of Cobalt in the Presence of Large Amounts of Nickel (Nickel Salts, Metallic Nickel)

a) Determination in Salts. 0.1—0.05 g* of the salt, containing from 0.03 to 1.0 mg of cobalt, is dissolved in water and the solution transferred to a separating funnel. The solution is acidified with 1 ml of HCl (1:1) and all the nickel and cobalt precipitated with 1 M potassium ethylxanthate. 10 ml of CCl_4 is added, and the contents of the funnel shaken vigorously until the xanthate complexes are dissolved in the organic solvent. The layers are allowed to separate and the CCl_4 layer transferred to another separating funnel. 20-30 ml of NH_4OH (1:1) is added to the xanthate complex solution and the funnel again vigorously shaken. When this is done, all the nickel goes into the aqueous phase as the ammine; iron, which may be present as a contaminant, forms ferric hydroxide while all the cobalt ethylxanthate remains in the organic solvent. After the layers have separated, the non-aqueous solution is run off, filtered through a dry filter, and its color intensity measured on a photocolorimeter, or on a colorimeter by the method of a series of standards. The solution of cobalt ethylxanthate is stable in the organic solvent, under water, for 3 days.

* When salts are analyzed which contain the anions of oxidizing agents (nitrate and nitrite ions), the aliquot is dissolved in water, 2-3 ml of H_2SO_4 (1:4) is added, the solution evaporated to white fumes of sulfuric acid, and the procedure described above then followed.

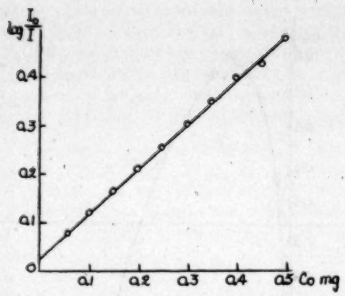

Fig. 3

When colors are measured in a photometer or photocolorimeter, the cobalt concentration is found by constructing a calibration curve beforehand (Fig. 3). Various amounts of a standard cobalt solution are used for constructing the latter, the aliquots being treated as described above.

A standard solution is prepared by dissolving 0.4769 g of recrystallized, air-dried, cobalt sulfate in water and diluting to 1 liter. One ml of such a solution contains 0.1 mg cobalt.

The method was checked by additions of various amounts of nickel sulfate. Results of determinations are given in Table 2.

TABLE 2

Mg cobalt added	0.00	0.05	0.20	0.50
Mg cobalt found	0.00	0.045	0.21	0.49

b) Determination of Cobalt in Metallic Nickel. Nickel in the form of turnings containing 0.03 to 1 mg cobalt, is dissolved in hydrochloric acid (1.19). When the aliquot has dissolved, a few drops of nitric acid (1.4) is added to destroy carbides, and the solution evaporated to dryness. The dry residue is moistened with hydrochloric acid, dissolved in water, and then the procedure described above in Section a followed. When cobalt was determined by this method in a standard sample of nickel (No. 91) containing 0.78% cobalt, the amounts found were 0.77, 0.78, and 0.79% Co. The method was also checked by the method of additions. Some of the results are given in Table 3.

TABLE 3

Cobalt content of a 0.16 mg aliquot of metallic nickel

Co added in mg	Total Co content in mg	Co found in mg
0.20	0.36	0.37
0.10	0.26	0.29
0.35	0.51	0.51
0.05	0.21	0.20

Determination of Cobalt in the Presence of Large Amounts of Iron

If cobalt is determined in the presence of large amounts of iron, according to the method outlined above, very low results are obtained. This is explained by the fact that on separating the xanthates with ammonia, a large precipitate of ferric hydroxide is formed, which traps both the aqueous and the non-aqueous phases on shaking.

An attempt to use oxalate as a complexing agent for iron during the isolation of cobalt ethylxanthate did not give positive results, since cobalt itself remains in the aqueous phase, under these conditions, as the oxalate complex.

Completely satisfactory results can be obtained for cobalt determinations if ammonium tartrate is used as a complexing agent for iron.

c) Determination of Cobalt in Iron-Nickel Ores.* 0.1-0.05 g of ore, containing from 0.03-1 mg of cobalt is placed in a small porcelain basin or beaker, worked up with 5-10 ml of aqua-regia and boiled for 5-10 minutes. 2-3 ml of H_2SO_4 (1:4) is then added and the solution evaporated to white fumes of sulfuric acid. The residue is diluted with water, the silica filtered off, the filtrate transferred to a separating funnel, and the procedure described above in a followed, with the difference that nickel and iron are not extracted with ammonia, but with an ammoniacal solution of ammonium tartrate. The method is suitable for the determination of cobalt in the presence of all the cations normally met, with the exception of large amounts of copper, mercury, and silver. Cobalt was determined in iron-nickel ores by this method. At the same time, the cobalt was determined in the same samples by the pyrophosphate-thiocyanate method of Zvenigorodsky [11].

Results of the determinations are given in Table 4.

* Gekht [4], has developed a colorimetric method for determination of cobalt in ore. In this method, the iron is kept in solution as the fluoride complex.

TABLE 4

Co found by the Zvenigarodsky method in %	0.02	0.07	0.26
Co found by the xanthate method in %	0.04	0.07	0.27

TABLE 5

Co added in mg	0.00	0.08	0.19	0.40
Co found in mg	0.00	0.09	0.21	0.42

d) Determination of Cobalt in Steels. 0.1-0.05 g of steel containing 0.03-1 mg of cobalt is placed in a 50-100 ml beaker and dissolved in HCl (1.19). After the aliquot has dissolved, a few drops of nitric acid (1.4) is added to destroy carbides and the whole evaporated to dryness. The dry residue is moistened with hydrochloric acid, dissolved in water, and the procedure described in c above followed.

This procedure was checked by the method of additions. Results obtained are given in Table 5.

SUMMARY

1. The solubility of ethylxanthates in some non-aqueous solvents (dichloroethane, $CHCl_3$, C_6H_6, CCl_4 and gasoline) has been studied.

2. It has been shown that the composition of the cobalt ethylxanthate complex corresponds to the formula $Co(C_2H_5OCS_2)_2$.

3. A method has been worked out for the colorimetric determination of cobalt in nickel, nickel salts, iron-nickel ores, and steels. The method is based on extraction of the xanthates of cobalt, nickel, iron, and others by CCl_4, after which the extract is treated with ammonia or a mixture of ammonia and ammonium tartrate, when the xanthates of the contaminating metals (Fe^{3+}, Ni^{2+}, and others) pass into the aqueous phase, while cobalt xanthate remains in the non-aqueous phase. The color intensity of the non-aqueous phase is proportional to the cobalt content. The sensitivity of the method is 0.03 mg Co in 10 ml of non-aqueous solution. It takes 10-15 minutes to carry out one determination after the test material has been dissolved.

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POLAROGRAPHIC DETERMINATION OF PLATINUM ON SOLID ELECTRODES. I

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Despite the fact that the polarographic determination of platinum and other metals of the platinum group is of considerable interest, few investigations have been devoted to this question.

Repin [1] studied the polarographic behavior of ions of di- and quadrivalent platinum on a mercury electrode. In order to avoid reduction of platinum ions by the anode mercury, the author used a pyridine complex of divalent platinum, which is stable to metallic mercury. He concluded that the possession of catalytic properties by the platinum metals, including platinum, excludes the possibility of using a polarographic technique for their analysis. Willis came to the same conclusion [2].

Englisch [3], explains Willis' lack of success by the fact that the latter only used divalent platinum, and points out that on working with quadrivalent platinum in neutral media, a clear cut reproducible wave with two horizontal branches can be obtained: the first at −0.6 V, the second at −0.8 V.

The height of the horizontal part is directly proportional to platinum concentration, and can be used for quantitative determinations. In order to maintain the media neutral, the author used a buffer solution consisting of citric acid and sodium hydrogen phosphate. Nevertheless, Englisch's paper does not contain a single curve and an arbitrary method of calculating the height of the wave is recommended. Since a steep rise starts at zero applied potential, while on reaching the value of the limiting current there is a rather weakly expressed inclined break, the author recommends the following method of calculation: the median line of the plateau pen oscillation should be determined; this line is extended back to intersect the 0.3 volt ordinate; the vertical distance from the starting line to this intersection point is then taken as the step height.

Miller [4], has pointed out the possibility of a direct polarographic determination of metals more noble than mercury on solid electrodes.

Lyalikov and Glazer [5], have developed a polarographic determination of silver on a solid electrode.

In the present instance, we have attempted to study the polarographic behavior of platinum on solid electrodes. Nobody has hitherto studied this problem.

The polarography of solutions of platinum on platinum electrodes is of interest from two points of view: 1) establishing the possibility of using a polarographic method for platinum, and, 2) clarifying the question of the influence of electrode polarization phenomena on the shape of the wave.

Several authors have pointed out the detrimental influence on the polarographic process of the new phase formed on the cathode – the deposit of the metal being determined. The polarographic waves are distorted and the electrode has to be depolarized. During polarographic determinations of platinum, we came up against the phenomenon of the formation of a new phase, which, in this particular case, is identical in nature to the electrode on which it has been deposited. There is, however, one difference: the character of the surface changes, the smooth surface of the electrode becomes covered with platinum "black" during electrolysis. The effect of cathode polarization should accordingly be different from that which is met during polarization of other metals.

EXPERIMENTAL

The work was carried out on a set-up * which we assembled ourselves. The mirror galvanometer had the

* This set-up can be used, if necessary, for recording over 2, 4 or 6 V ranges, and also, by the use of the requisite switches, for operating over cathodic and anodic regions.

following characteristics: an M-21 galvanometer with an oscillation period of 4 seconds on open circuit, inner critical resistance 1,000 Ω, constant with respect to a current 10^{-9} A/mm, and with an additional internal resistance of 5,000 Ω, shunted with an Ayrton system. A platinum needle 5 mm long and 0.5 mm in diameter served as a cathode; the anode was a platinum plate with an area of 150 mm^2.

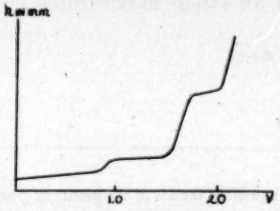

Fig. 1. Polarographic wave of platinum.

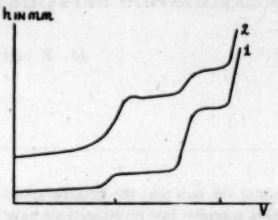

Fig. 2. Waves of platinum: 1) after passing nitrogen; 2) after the solution has stood in the air for 24 hours.

A standard platinum solution was prepared by dissolving a known weight of platinum chloride in water. The concentration of the standard solution was determined gravimetrically, by precipitating platinum as potassium chloroplatinate. 0.1 N sodium nitrate was used as supporting electrolyte. A known volume of platinum solution (T = 0.0012) was introduced into the electrolyzer, and made up to 25 ml with supporting electrolyte. All the results in the present work were carried out with a galvanometer sensitivity of 1/200.

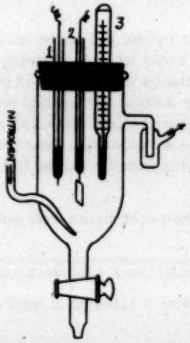

Fig. 3. Electrolyzer: 1) cathode; 2) anode; 3) thermometer.

TABLE 1

Experiment No.	Platinum concentration in g	H_1 * in mm	H_2 in mm
1	0.0008	4	23
2	0.0008	4	24
3	0.0008	4	23
4	0.0008	4	24
5	0.0008	3	24
6	0.0008	4	24
7	0.0008	4	26
8	0.0008	4	25

* H_1 – height of the first wave; H_2 – height of the second wave.

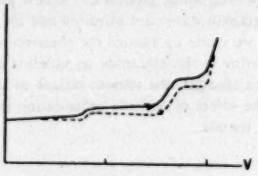

Fig. 4. Waves for the forward and reverse directions.

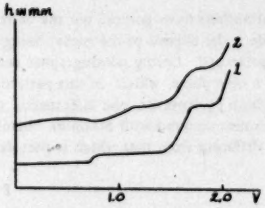

Fig. 5. Waves of platinum: 1) on a smooth electrode; 2) on a platinized electrode.

Polarization curves were obtained on this set-up using $NaNO_3$ as supporting electrolyte (Fig. 1). The polarogram shows two well defined diffusion waves at potentials of 0.6-0.7 V and 1.6-1.7 V.

The height of the second wave, is 4-6 times the height of the first wave, according to concentration. The presence of any dissolved oxygen in the solution is a great hindrance to getting clearly defined waves. Only after careful removal of oxygen from solution by blowing nitrogen through it for not less than 45 minutes were good waves obtained.

Tests showed that even traces of oxygen distorted the shape of the waves obtained. The nitrogen was therefore passed over copper at 500° before being passed through the solution. Fig. 2 illustrates curves obtained before and after passing nitrogen through the platinum solution. and also a polarogram for a solution of platinum which has once been freed from oxygen and then allowed to stand in air again. On passing nitrogen through a second time, clearly defined waves are obtained once more. In view of what has just been said a special cell protected from exposure to the air was used (Fig. 3).

The half wave potentials determined from the graph

$$E - \log \frac{i}{i_d - i}$$

have the following values: 0.85 V for the first wave, and 1.65 V for the second wave. It should be noted that the slope of the straight lines in the system exceeds the theoretically possible values by a considerable amount; thus, for the first wave it is equal to 0.062 and for the second 0.083. This indicates that the processes which occur on the electrode are irreversible.

Our experiments showed that, in contrast to all other known cases of polarography with solid electrodes, in the case of platinum the phenomena of electrode polarization, within known limits, has no effect on the value of the diffusion current.

Table 1 contains the results obtained on taking polarization curves of the same solution of platinum and the same electrodes without cleaning the surface.

As is evident from the table, all the eight polarograms which were taken successively indicate that the value of the diffusion current of both the first and the second wave remains constant; the shape of the wave is also well maintained. In order to define the effect of polarization, curves were taken in the forward and reverse directions. As Fig. 4 shows, the polarograms obtained in both direct ions almost coincide: in each case the shape of the polarograms and the wave heights are the same.

In order to have more information on the effect of electrode polarization, polarograms were taken of a platinum solution on a platinized cathode. The cathode was immersed in a 2% solution of chloroplatinic acid, and the solution electrolyzed for 30 minutes; the cathode is covered with a film of platinum "black" by this process. As can be seen from Fig. 5, the polarograms obtained on a smooth electrode are more clearly defined, the steps are better expressed, and it is easier to measure the wave height. On the second polarogram, an increase in the first and a decrease in the second wave are observed.

There is probably a definite limit, and when this limit is reached, the thickness of the layer of friable platinum which has been deposited on the cathode starts to distort the shape of the curve.

The effect of the temperature coefficient on the value of the diffusion current was also studied. The temperature coefficient for the first wave was found to be ca.6%, and for the second wave ca.2% per degree.

In order to check on the possibility of using this method for the quantitative determination of platinum, polarograms were taken of platinum solutions of varying concentrations. As the calibration curve shows (Fig. 6), there is a linear relation between concentration and wave height both for the first and second curves.

In order to economize on platinum solutions, we checked on the possibility of using small volumes of platinum solutions. With this aim in view, a micro-electrolyzer was constructed (Fig. 7), in which the anode, in the form of a flat annulet, was fused into the lower part.

0.1 ml of the platinum solution was measured out with a micropipet, and made up to 1 ml with supporting electrolyte. As Fig. 8 shows, clear cut polarograms are obtained by means of which it is possible to determine platinum concentrations of the order of 10^{-4} g/ml.

An attempt to titrate platinum amperometrically with a solution of potassium chloride in an alcoholic medium

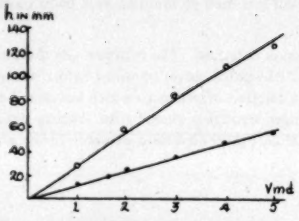

Fig. 6. Calibration curves using the first (⊘), and second wave (O); V - volume of solution in ml; T_{Pt} = 0.0012 g/ml.

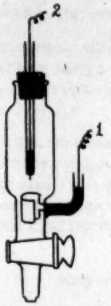

Fig. 7. Micro-electrolyzer 1) anode; 2) cathode.

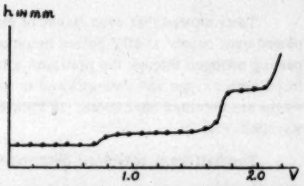

Fig. 8. Wave for platinum obtained in the micro-electrolyzer (volume of solution 1 ml containing 0.00066 g)

was unsuccessful. Apparently the solubility of the potassium chloroplatinate is too high, the platinum wave decreases slightly, but does not fall to zero.

SUMMARY

1. It has been shown that on taking polarograms of aqueous platinum chloride solutions two waves are obtained; the first at a potential of 0.7 V, the second at a potential of 1.6 V.

2. The diffusion current for both waves is proportional to concentration, so that platinum can be determined quantitatively by means of it.

3. Electrode polarization in the case of polarographic studies of platinum solutions, in contrast to other cases, has no effect, within certain limits, on the shape of the wave and on the value of the diffusion current.

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POLAROGRAPHIC DETERMINATION OF ETHYLNITRATE AND ETHYLNITRITE IN AQUEOUS SOLUTIONS

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The polarographic method has found wide application for both qualitative and quantitative analysis of organic compounds in all branches of chemistry and chemical industry. At present there is a very large list of materials for which an accurate polarographic method of analysis has been worked out. In the literature on the class of compounds containing the nitro -(NO_2), and nitroso-(NO) groups respectively, it is possible to find information on the polarographic analysis of nitro paraffins [1, 2], nitrobenzene [3, 4], nitrophenol and nitraniline [5], picric acid [6], nitrocatechol [7], nitromesitylene [4], trinitrotoluene [8], and others. The polarographic reduction of inorganic nitrates and nitrites has also been studied [9].

Hitherto, little or no information has been published on the polarographic analysis of nitric acid esters. Only the half-wave potentials of n-butyl nitrate and various non-aqueous solvents have been determined [10].

The present article is devoted to a study of the conditions necessary for the polarographic determination of ethylnitrate and ethylnitrite in aqueous solution.

Original Materials. Ethylnitrate was synthesized from absolute ethyl alcohol and concentrated nitric acid in the presence of urea nitrate [12]. The product obtained was distilled twice with permanganate and the fraction boiling between 85.5 and 86° at 750 mm of mercury chosen. The refractive index was $1.3846^{21.5}$ (published results: boiling point 86°; refractive index $1.3848^{21.5}$).

Ethylnitrite was synthesized from an aqueous solution of $NaNO_2$, ethyl alcohol and concentrated hydrochloric acid [11]. The distilled product boiled at 17°, the figure given in the literature.

Electrolytic Reduction of Ethylnitrate and Ethylnitrite. Reduction of ethylnitrate and ethylnitrite on the dropping mercury cathode was studied in various media (LiOH, LiCl, HCl). Dissolved oxygen cannot be removed from solution in these cases by passing an inert gas through the solution since the ethylnitrate and ethylnitrite will also be removed. Consequently, both the electrolyte and the water used for preparing the test solutions were freed from oxygen separately, and kept in a hydrogen atmosphere before use. Before actually taking a polarogram, 0.2-0.3 ml of test solution was introduced into the electrolytic cell containing the electrolyte, by means of a micro-pipet to which the air has no access.

Analysis was carried out on a polarograph made by the Leningrad factory "Geologorazvedka"; the polarograms are recorded photographically in this machine. Polarograms obtained during electrolytic reduction of ethylnitrate and ethylnitrite are reproduced in Figs. 1 and 2. Fig. 2 also illustrates the extent to which the solutions are free from oxygen.

The values which we obtained for the half-wave potentials in various solutions, with respect to the normal calomel electrode are collected in Table 1.

It follows from the results given in this table that the half-wave potentials of ethylnitrate and ethylnitrite are practically independent of pH. In acid media (0.1 N HCl) reduction occurs at the same potential. All the same, clearly defined waves were not obtained. This is related to the fact that in the presence of ethylnitrate and ethylnitrite, the reduction potential of hydrogen ions is strongly shifted to less negative values, and the polarographic waves for these two compounds fuse into the reduction wave for H^+.

When polarograms were taken of solution containing both ethylnitrate and ethylnitrite, only one curve was obtained, despite the appreciable difference in the half-wave potentials of the two compounds. The waves can be

TABLE 1

Half-wave potentials with respect to the normal calomel electrode in volts

Material	0.1N LiOH $E_{1/2}$	0.1N LiCl $E_{1/2}$	0.1N HCl (at the start of reduction)
Ethylnitrite	−0.94	−0.96	−0.7
Ethylnitrate	−0.65	−0.70	−0.5

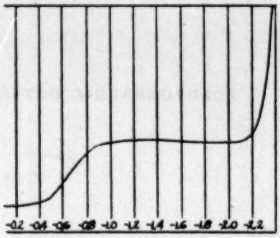

Fig. 1. Polarogram of a solution of ethylnitrate ($C_2H_5ONO_2$) in 0.1 N LiOH

separated (Fig. 3) by changing the scale of the voltage axis, i.e., when the polarograms are taken at a potential of 2 V instead of the customary 4 V across the ends of the potentiometer bridge. Nevertheless, even when this technique is tried, separation of the two waves is not good enough.

In order to check on the values found for the half-wave potentials, a few drops of 0.01 N thallium sulfate, whose half-wave potential of 0.49 V (with respect to the normal calomel electrode) is independent of the composition of the solution, was added to a test solution [12]. The first wave on Fig. 3 corresponds to the reduction of thallium ions.

Effect of Additions of Certain Organic Compounds. Qualitative determination of ethylnitrate and ethylnitrite by means of their half-wave potentials is complicated to a considerable extent by the sensitivity of their reduction process to the presence of certain organic materials, even in very small amounts, in the test solution. Since more often than not one has to deal with solutions of these materials and not the pure materials themselves, the effect of solvents is most important.

During a study of the electrolytic reduction of ethylnitrate and ethylnitrite in aqueous solutions containing ethyl alcohol, we found a very strong relation between the half-wave potentials and the amount of alcohol added. The polarographic curve in Fig. 4 shows the displacement of the half-wave potential of ethylnitrate in the presence of 35% ethyl alcohol.

At lower alcohol concentrations, the potential shift is less; addition of more than 40% alcohol does not lead to a further potential shift (Table 2).

Diethyl ether has an even greater effect on the half-wave potentials of ethylnitrate and ethylnitrite. With increasing ether concentration in the test solution, the half-wave potential of ethylnitrate is shifted to −1.3V and that of ethylnitrite to −1.4 V.

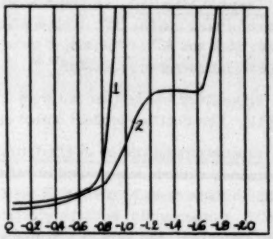

Fig. 2. Polarograms of ethylnitrite solution (C_2H_5ONO): 1—in 0.1 N HCl; 2—in 0.1 N LiOH

We also studied the electrolytic reduction of ethylnitrate and ethylnitrite in the presence of gasoline (since there are indications in the literature [13] that these materials are used as additives for diesel fuels) and methyl alcohol. In both cases no shift in the half-wave potentials was observed.

In the paper by Gray [14], on the photolysis of ethylnitrate, it is pointed out that the reduction potential of acetaldehyde is shifted in the presence of ethylnitrate. Our experiments (Fig. 5) indicate no such shift in the half-wave potential of the aldehyde in aqueous solutions containing ethylnitrate. Simultaneous determination of aldehydes and ethylnitrate is therefore quite possible.

Ethylnitrite in solution does not affect the reduction potential of acetaldehyde either (Fig. 6). In this case, however, polarographic determination of the aldehyde is complicated by the fact that in the presence of ethylnitrite, the reduction potential of lithium ions is strongly shifted to less negative values (Fig. 2), so that the polarographic waves of the aldehyde and lithium fuse.

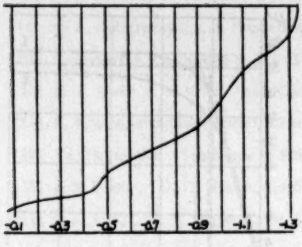

Fig. 3. Polarographic determinations of ethylnitrate and ethylnitrite when they are both present together.

Polarogram in a supporting electrolyte of 0.1 N LiOH in the presence of Tl^+ ions.

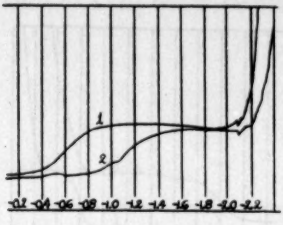

Fig. 4. Potential shift of the half-wave potential of ethylnitrate in the presence of ethyl alcohol.

Polarograms of ethylnitrate: 1) in 0.1 N LiOH; 2) in the same solution in the presence of 35% C_2H_5OH.

Thus, in studying the conditions for the polarographic determination of nitric acid esters in aqueous solutions, one must take into account the possibility of a shift in the reduction potentials both of the esters themselves (because of the presence of certain organic materials), and of other compounds in the solution (because of the presence of nitric esters).

TABLE 2

Half-wave potentials of ethylnitrate in aqueous-alcohol solutions in volts.

% Ethyl alcohol	0	13.8	24.0	32.4	39.0	42	50
$-E_{1/2}$	0.65	0.86	1.02	1.07	1.2	1.2	1.2

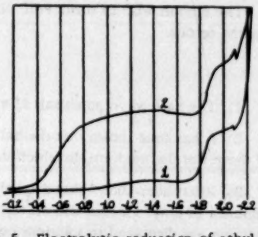

Fig. 5. Electrolytic reduction of ethylnitrate in the presence of acetaldehyde:

1) solution of CH_3CHO in 0.1 N LiOH;
2) the same solution in the presence of ethylnitrate.

Quantitative Determination

Solubility Determination. The solubility of ethylnitrate and ethylnitrite in water is high enough for the quantitative polarographic determination of these compounds. Ethylnitrite hydrolyzes strongly on dissolving in water; nevertheless, the rate of hydrolysis in the presence of weak alkali is slowed down appreciably. Thus, on dissolving ethylnitrite in 0.1 N LiOH at 0°, the height of the polarographic wave hardly changes at all on standing for half an hour. Accordingly, the quantitative polarographic determination of ethylnitrite in aqueous solutions in an alkaline medium is quite possible. The linear relation between the values of the diffusion current and concentration of ethylnitrate and ethylnitrite respectively, is maintained in a fairly wide range of concentrations, and only breaks down near the solubility limit.

On taking the temperature up to 50°, the linear relation between diffusion current and concentration is maintained.

We determined the solubility of ethylnitrate in water from the deviation in the linear relation between the values of the diffusion current and ester concentration.

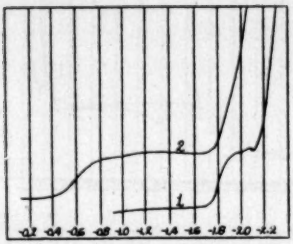

Fig. 6. Electrolytic reduction of ethylnitrite in the presence of acetaldehyde:

1) Solution of CH_3CHO in 0.1 N LiOH;
2) the same solution in the presence of ethylnitrite.

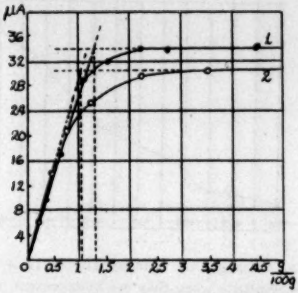

Fig. 7. Relation between diffusion current and ethylnitrate concentration.

Determination of ethynitrate solubility in water: 1) at 20°; 2) at 50°.

Solubility is defined as the coordinates of the point of intersection of the straight line which corresponds to the relation between diffusion current and concentration, and the horizontal corresponding to the saturation region (Fig. 7).

The method which is suggested for determining solubility is characterized by the high degree of accuracy possible using a polarographic technique, and may find application in a number of other cases.

The authors wish to thank Prof. N. M. Emanuel for his help and guidance in carrying out the work, and discussing the results.

SUMMARY

1) The half-wave potentials of ethylnitrate and ethylnitrite have been determined in aqueous solutions.

2) It has been shown that the half-wave potentials of ethylnitrate (−0.7), and ethylnitrite (−0.96) are independent of the pH of the medium, in which the reduction is carried out.

3) It has been shown that $E_{1/2}$ of ethylnitrate and ethylnitrite vary within appreciable limits, according to the presence of ethyl alcohol and diethyl ether in the system. The reduction potentials of lithium and hydrogen ions respectively are displaced in solutions containing ethylnitrite.

4) A polarographic method is proposed for the determination of solubility. The solubility of ethylnitrate in water has been determined by this method.

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POTENTIOMETRIC METHODS OF INVESTIGATING HIGH MOLECULAR WEIGHT COMPOUNDS OF PETROLEUM

I. POTENTIOMETRIC DETERMINATION OF ACIDITY

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Indicator methods of determining the content of acids, peroxides, and unsaturated compounds are widely used for characterizing the chemical nature of organic compounds. Nevertheless, indicator methods of titration, which are readily applied to low molecular weight compounds, in the majority of cases of uncolored organic compounds, are not applicable to a study of more complex, intensely colored organic products, of which petroleum, petroleum resins, shale and coal resins, asphalts, etc., are typical. In recent years therefore there has been an increasing tendency to switch over from indicator to potentiometric methods of titration, which give more objective and accurate results as compared with indicator methods. Work has started to appear on the application of potentiometric titration to both the study of light petroleum products, and the standardization of these methods, [1]. Hitherto, no reliable work has appeared on the application of potentiometric titration to a study of intensely colored complex organic compounds, of which resin solutions are examples.

Since we have to deal with intensely colored, high molecular weight compounds, of petroleum (resins, asphaltenes) which are insoluble in water and the lower alcohols, it was thought desirable to switch over to the use of potentiometric methods of titration, which seemed to use the most reliable and accurate method of characterizing chemically active groups of atoms entering into the composition of complex molecules. In this connection therefore, we made a preliminary survey of methods in order to work out potentiometric methods of determining unsaturatedness, acidity, and also peroxides, and saponifiable compounds in solutions of petroleum resins, petroleum, and heavy petroleum residues.

This article is the first of a series of studies which we have carried out on the application of potentiometric methods to the study of petroleum resins and other colored petroleum products.

Determination of the Acid Numbers of Resins

Before acidity can be determined the test material has to be dissolved in some solvent. Resins dissolve readily in benzene, dichloroethane, carbon tetrachloride, chloroform, and some of the mixtures of these solvents with alcohols. Solutions of resins in these media have a high internal resistance, so that if potentiometric determinations are to be carried out on them, tube amplifiers are necessary. We used the LP-5 and Moskip P-3 potentiometers in conjunction with a LU-2 amplifier.

The acid number, i.e. the number of milligrams of KOH used to neutralize the acid in 100 g of test sample is calculated according to the formula:

acid number = VT/g, where V – is the volume of KOH used to titrate the acids; T – the titer of KOH; g – the weight of resin.

It is very difficult to determine the end point of colored products such as petroleum and resins by means of an indicator. The potentiometric method of determining acid numbers in petroleum has not been checked on resins. Resins, which are essentially complex mixtures, can lead to complications.

According to the GOST* methods 1784–47, titration with an aqueous alkali solution is carried out until the E. M. F. is zero, i.e. when the potential of the indicator electrode is the same as that of the standard half element reference electrode. Determination of acidity is carried out in an alcohol-benzene mixture. Such measurements are not suitable, since titration to a potential determined beforehand is only possible if the same mixture is always

* GOST = All-Union State Standard.

used as the solvent. When the solvent is changed it is essential to change the standard electrode as well (the reference electrode).

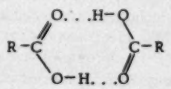
The use of aqueous alkali for titration of petroleum products leads to separation of the system into layers, which is always accompanied by a certain non-reproducibility of results. We have made various modifications to this method in order to eliminate this drawback.

In choosing a solvent we were guided by the following considerations: the solvent must dissolve petroleum products, including resins, and the solution thus obtained should have a sufficiently high electrical conductivity. The most suitable solvent would be one which would not necessitate the use of an amplifier. Examples of solvents which could fulfill this requirement are the basic solvents (pyridine, hydrazine, etc.); in such solvents however, it is impossible to use the most popular indicator electrodes. Moreover, it has been known for a long time that pyridine not only acts as a solvent, but as a chemical reagent for resins. A number of materials which themselves do not possess acid properties exhibit such properties in basic solvents.

The lower alcohols cannot be used as solvents, since they are poor solvents for petroleum and resins.

The best solvents for petroleum products are benzene, carbon tetrachloride, and dichloroethane (aprotonic solvents). Benzene has the added advantage that it is widely used in all laboratory and factory work. Even in dichloroethane, which has the highest dielectric constant, the electrical conductivity of acids is so small that the use of available amplifiers is insufficient for carrying out measurements. The use of various non-aqueous solvents modifies acid strength and titration conditions considerably [2].

An acid can only exhibit its acid properties when another material is present – a base, which can accept the protons liberated by the acid. This substance, in the case of hydroxyl-containing, and a number of other solvents, is the solvent itself. According to Brönsted's theory, the greater the capacity of the solvent-base to combine with a proton, the stronger the acid dissolved in it will be. In aprotonic solvents, however, proton transfer is excluded, so that acids exhibit acid properties by donating the proton either to an added base or to another molecule similar to itself. As spectrophotometric [3], and cryoscopic results [4], show, molecules of carboxylic acids are found in the form of dimers of the following type:



in aprotonic solvents.

Such a dimer can split up to form ions of the type $RCOO^-$ and $RCOOH_2^+$. It is completely obvious that the number of such ions will be insignificant, and that their number will be smaller the lower the dielectric constant, i.e acids will be weak in aprotonic solvents.

The weaker the acid, the less accurate the titration: this follows from Roller's formula [5],

$$\epsilon = \pm 200 \sqrt{K} \sin h\Delta,$$

where Δ is the error in determining the end point (equal to 0.158Δ mV during potentiometric titration and 0.58Δ pH for indicator titrations); sin h is the hyperbolic sine; K, a factor related to the dissociation constant of the acid and the ionic product of the medium as follows:

$$K = \frac{K_i}{K_a C_a}$$

(for titration of a weak acid with a strong base).

The ionic product of the solvent K_i is very small in this instance, which should mean that conditions are favorable for titration; the lower value of the dissociation constant of the acid K_a, however, more often than not, covers up this effect. It was essential, therefore, to choose an additive for an aprotonic solvent which increases the acid strength to a maximum. Alcohol is used as the additive in GOST methods. In an alcohol-benzene mixture, titration will improve because of the decrease in the ionic product of the alcohol (because benzene is present), and of an increase in acid strength compared to that in benzene alone (because of the addition of alcohol). An alcohol-benzene solution of acid will act as if conducting ions similar to alcohol were present, but with a modified ionic product and dielectric constant.

The higher the percentage of benzene in the mixture, the better the titration conditions. We titrated a strong acid, HCl, in alcohol-benzene mixtures, using various ratios of alcohol to benzene, and became convinced that this was the right choice.

On increasing the amount of benzene beyond the optimum, the mixture became gel-like and titration became difficult, and sometimes even impossible. Alcohol-benzene mixtures containing from 25-50% alcohol proved to be the best. We used mixtures of 2:5 and 1:1. The most suitable is a 2:5 mixture, since during titration with alcoholic potash, the amount of alcohol increases, and at the equivalence point reaches 50%.

For preparing the solvent mixture, as is evident from Table 1, alcohol and benzene of various degrees of purity were used (technical benzene, redistilled benzene, cryoscopic benzene, and alcohol, alcohol treated with alkali, rectified spirit, etc.). Other solvents, such as acetone, dichloroethane-alcohol, carbon tetrachloride-alcohol were also tried. The mixture of dichloroethane-alcohol (in a 2:5 ratio) can also be used as a solvent without using an amplifier. When this solvent was used saturated with LiCl, a Moskip P-3 potentiometer was used which had a sensitivity of 2-3 mV.

TABLE 1

Comparison of the acid numbers obtained for resins from Ilsky petroleum when solvents of varyious degrees of purity were used

Resin sample number	Purity of solvent	Weight taken, in g	Acid number
135	Cryoscopic benzene	0.1030	55.7
		0.1127	55.1
		0.0911	56.3
175	Alcohol, distilled over KOH	0.3112	16.6
		0.3378	16.7
135	Rectified spirit	0.0733	55.1
		0.0950	55.1
		0.0835	57.5
175	Technical benzene	0.2701	16.8
		0.4500	17.1
		0.3112	16.6
135	Cryoscopic benzene	0.0696	56.3
175	Redistilled alcohol	0.4373	16.8
		0.4381	16.4
		0.3599	16.7

Acetone and carbon tetrachloride were used because they are solvents for individual resin fractions.

We checked on the suitability of the most widely used electrodes, which are reversible with respect to hydrogen ions, for measurements in the media we used.

The hydrogen gas electrode, antimony, glass, and quinhydrone electrodes, etc., can be used as indicator electrodes for hydrogen ions. The suitability of these electrodes for determination of acids in alcohol-benzene mixtures was also checked. An antimony beaker was used as an antimony electrode; it proved unsuitable for determination of acidity in petroleum products; its potential changed with time, and depended on agitation, preliminary treatment of the surface, etc.

The hydrogen gas electrode is not suitable under ordinary laboratory conditions.

The potentials of the quinhydrone and smooth platinum electrodes, respectively, are stable enough and are easily reproducible. Preference was given to a smooth platinum electrode, since it does not necessitate the introduction of other additives into a titrant mixture, which is already complex enough.

The potential of the glass electrode is also reproducible and is rapidly established; the only snag with this electrode is its fragility, but if it is handled carefully, a glass electrode in conjunction with a tube potentiometer can be operated for a long time.

In preparing a new electrode, or using a new solvent, it is essential to check on the linearity of the relation between E.M.F and hydrogen ion concentration. A check on the behavior of a glass electrode in an alcohol-benzene mixture shows that in solutions with concentrations from 1 N acid to 1 N alkali, there is a linear relation between potential and pH, and that this line has the theoretical slope.

Thus, we finally decided on smooth platinum and glass electrodes, respectively, as indicator electrodes and a saturated calomel electrode as reference electrode, though a silver chloride or any other reference electrode can be used successfully. The important factor is that the potential of the reference electrode should be constant and reproducible.

The electrolytic circuit was made up of a siphon with a saturated aqueous solution of KCl. The whole set-up can be represented as follows:

$$\text{Pt} \;\Big|\; \begin{matrix}\text{Solution of resin}\\ \text{in alcohol-benzene}\end{matrix} \;\Big|\; \begin{matrix}\text{KCl}\\ \text{saturated}\end{matrix} \;\Big|\; Hg_2Cl_2 \cdot Hg$$

A 0.05 N alcoholic solution of alkali was used as titrant.

Analytical Procedure. 0.1 g of test material is dissolved in 10-15 ml of alcohol-benzene mixture. The solvent mixture is prepared beforehand by mixing alcohol and benzene in definite proportions; sometimes the test material dissolved very slowly. In these cases it is best to dissolve it in benzene alone and then add the alcohol. Beaker plus solution is covered with a ground glass cover, through which pass the indicator electrode, siphon, the tip of the buret containing titrant, and a stirrer (we used a bubbler instead of a stirrer). The calomel electrode is connected via siphon with the KCl. The general appearance of the test cell is shown in Fig. 1.

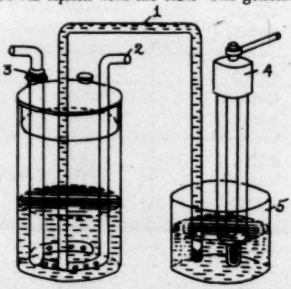


Fig. 1. General view of the cell used for titration. 1) Siphon with saturated KCl solution; 2) bubbler; 3) platinum electrode; 4) calomel electrode; 5) beaker plus saturated KCl solution.

Wires from the indicator and reference electrodes are, respectively, connected to the potentiometer, and other operations carried out as usual. When the initial potential has been determined, a small aliquot of the alkali solution is added and the potential measured again. The volume of alcoholic alkali is plotted (graphically) against E.M.F., (Fig. 2).

The equivalence point, which is given by the volume of alkali used for titrating free acids in the aliquot taken, is found from the curve. Since the amount

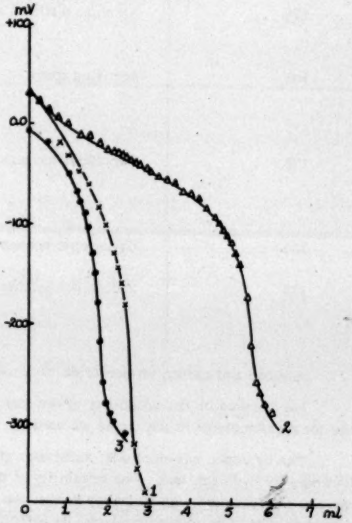


Fig. 2. Titration curves
1) Benzoic acid; 2) 0.1111 g resin No. 135 to which benzoic acid has been added; 3) 0.0835 g resin No.135 without addition of benzoic acid.

of acids in the resins can be very small, the acidity of the resin and of the solvent itself may be of the same order so that errors in determinations can be very high. In such cases it is essential to determine the acidity of the solvent alone.

The acidity of the solvent itself is determined in the same way as that of the resin, the only difference being, of course, that no resin is added to the solvent. Alkali solution is added dropwise. Determination of the acidity of the solvent itself can often be very difficult. Since only a few drops of alkali is required for neutralization of the solvent, very steep curves are obtained, from which it is difficult to determine the maximum slope; it is best, therefore, to carry out titration to a definite potential (corresponding to the potential at the equivalence point during titration of the test sample).

One must remember that when carrying out such titrations there is a possibility of mistakes arising from the fact that the potential at the equivalence point differs with acids of various strength. The weaker the acid being titrated, the lower the potential at the equivalence point. This phenomenon is observed in any solvent; in aqueous solutions during titration of hydrochloric acid, the pH at the equivalence point coincides with the neutralization point and is equal to 7, but on titrating acetic acid the equivalence point lies at a pH of 9.

Only if the acids in the solvent and in the resin solution are similar in strength, does such titration give correct results. Much better results are obtained if the following technique is used: a small amount of some weak acid, e.g., benzoic acid, is added before titration. This solution is then potentiometrically titrated. The amount of alkali used for neutralization will include the alkali which has been spent in neutralizing the acids already present in the solvent. An aliquot of resin is then dissolved in a prepared solution of benzoic acid, and titration carried out as before.

As can be seen from the results given in Table 2, such a technique gives results which are in fairly good agreement with each other.

A graph is constructed relating the E.M.F. in millivolts to the volume of alkali added. The curves which are obtained are always similar to the curves in Fig. 2, and from them the amount of alkali used to titrate the resin can be determined.

By constructing a curve for the titration of the solvent it is possible to find the volume of alkali used for titrating the solvent on its own, and knowing this one can determine the amount of alkali used to titrate the aliquot of sample.

TABLE 2

Determination of acid numbers of Ilsk petroleum resin in the presence of standard additions of acid

Resin sample number	Weight of aliquot, in g	Acid number
135	0.0621	56.5
135	0.0696	56.3
135	0.1110	56.5
175	0.2427	16.9
175	0.4262	17.1
172	0.2510	9.0
172	0.2435	9.2

As can be seen from Table 3 the results obtained are good enough. Potentiometric methods always give more accurate results, so that it is better to use them not only for colored solutions, but also in uncolored solutions, where indicator methods could be used.

Table 4 contains results of determinations of the acid numbers of Turkmenian and Tuimazinsky petroleum, carried out potentiometrically and by indicator methods. The results obtained potentiometrically usually exhibit better reproducibility than those obtained by means of an indicator.

TABLE 3

Acid numbers of several samples of Ilsk petroleum resins

Resin sample number	Weight of aliquot, in g	Volume of alkali used for titration (ml) (N_{alkali} = 0.0382)	Acid number	Notes
	0.0911	2.40	56.3	
	0.1030	2.68	55.7	Smooth Pt-electrode
	0.1127	2.90	55.1	
	0.1149	2.98	55.5	Glass electrode
135	0.0835	2.25	57.3	Alcohol and benzene – unpurified
	0.0733	1.89	55.1	Smooth electrode
	0.0950	2.45	55.1	Smooth Pt electrode
	0.0709	1.82	54.9	Quinhydrone electrode
	0.0621	1.64	56.5	Titration carried out in the presence of
	0.0696	1.83	56.3	benzoic acid
	0.1110	2.93	56.5	
	0.4373	3.44	16.8	
	0.4481	3.36	16.4	
	0.3599	2.83	16.1	Alcohol and benzene – unpurified
	0.2707	2.13	16.8	
175	0.4500	3.60	17.1	
	0.3112	2.33	16.0	
	0.3378	2.64	16.7	Titration carried out in the presence of benzoic acid
	0.2427	1.92	16.9	
	0.4262	3.46	17.3	
	0.2033	0.93	9.8	Glass electrode
172	0.2510	1.055	9.0	In the presence of benzoic acid
	0.2435	1.05	9.2	Pt-electrode under the same conditions
	0.2251	1.01	9.6	
	0.2405	1.68	14.9	
139	0.2113	1.43	14.5	
	0.0860	0.44	10.9	
193	0.1455	0.70	10.3	

TABLE 4

Comparison of acid numbers of different fractions of resins from Turkmenian and Tuimazinsky petroleum obtained potentiometrically and by indicator methods

Resin sample	Indicator method	Potentiometric method	Resin sample	Indicator method	Potentiometric method
Tuimazinsky Petroleum			Turkmenian petroleum		
Total resinous materials	7.1; 7.4	8.4	Total resinous materials	22.7; 21.4	23.46; 23.98
Fractions, desorbed by CCl_4 *	1.3	1.43; 1.32	Fraction, desorbed with CCl_4	3.4	3.6
Fraction, desorbed with C_6H_6	5.3; 5.2	5.39; 5.38	Fraction, desorbed with C_6H_6		9.13; 8.58
Fraction, desorbed with CH_3COCH_3	10.4	10.03; 9.95	Fraction, desorbed with CH_3COCH_3	65.8; 62.6	68.5; 69.15

* The fractions of petroleum resins were obtained by adsorption of the resins on silica gel, from which they were subsequently removed with various solvents in the following order: CCl_4, C_6H_6, CH_3COCH_3, alcohol-benzene mixture in the ratio 1 : 1 [6].

SUMMARY

1. Optimum conditions have been found for the potentiometric determination of acidity in non-aqueous solutions of complex mixtures of organic compounds.

2. The applicability of the most common indicator electrodes for determination of acidity in alcohol-benzene solutions has been experimentally investigated, and it was shown that platinum and glass electrodes are most suitable for this purpose.

3. A method is proposed for potentiometric determination of acid numbers of petroleum resins.

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF HALOGENS IN ORGANIC MATERIALS

I. QUANTITATIVE DETERMINATION OF CHLORINE, BROMINE, AND IODINE

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There are many quantitative methods of determing halogens in organic materials [1]. Most of them are based on complete oxidative or reductive breakdown of the molecules of organic material. Under such conditions, the halogens which enter into the composition of the organic material are liberated in a free state or in the form of hydrogen halides, or as a mixture of free and combined simultaneously (and in the forms of compounds corresponding to them). Each of these methods has its advantages, disadvantages, and fields of application.

Recently, some analysts have turned their attention to reduction methods, particularly to the fusion of test material with metallic potassium [1], or magnesium powder [2].

Of great practical interest is the method of determining halogens based on oxidation of the organic material by heating in a stream of oxygen [3]. Some of the fundamental drawbacks of this otherwise good method are the necessity of using platinum catalysts, the length of time required to carry out an analysis, etc. This method can be simplified by raising the decomposition temperature of the material inside the combustion tube, and increasing oxygen throughput, so that one can do without platinum catalysts, and at the same time speed up the rate of decomposition of the organic material. Nevertheless, when this technique is tried, a cloud is formed consisting of halogens, water vapor, and hydrogen halides, and at the high throughput used, all the materials are not completely adsorbed by the absorbent. In order to overcome this trouble of the formation of a cloud of decomposition products, various methods have been suggested [4], some of which have led to positive results.

In the present article we describe new methods for the quantitative determination of halogens in organic materials which have a number of positive, new features. Our methods are based on combustion of the halogen containing organic material in a rapid stream of oxygen (150-200 ml/ minute) at a temperature of 800-900° without using a catalyst.

The complex question of overcoming the difficulties associated with the formation of a cloud of decomposition products was solved very simply: a small glass tube containing fine crystalline powder was connected to the combustion tube; this crystalline powder may be composed of various materials; e.g., bromides, chlorides, iodides, etc.

On passing through such a filter tube, the cloud is held back, broken down, and the material then acquires its usual form, and is easily absorbed by aqueous solutions.

The use of this filter tube enabled us to develop new and improved methods for the quantitative determination of halogens. The following are the advantages of the new methods:

1) the decomposition rate of test material is speeded up;
2) there is no need for expensive catalysts;
3) cloud formation is stopped and more rapid and quantitative trapping of halogens and hydrogen halides by the aqueous solutions is achieved.

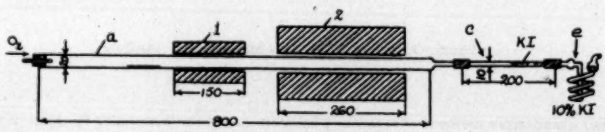
The second part of the analysis – quantitative determination of halogens in the absorbent – does not present any complexities. This problem was solved long ago by analytical chemists. The halogens absorbed by the absorbent can be determined by one of the well known methods described in the literature – gravimetric or volumetric. In order to check the method, we decided on the biiodate method of determining halogens as being more simple, rapid and convenient, and also sufficiently accurate (±0.1–0.2%).

The iodometric method of determining iodine based on oxidation of iodine liberated by bromine to periodic acid, which is used in microanalysis, has no essential advantages in semi-micro and macroanalysis, because of the length of time it takes to carry out an analysis, and the necessity of carrying out a number of supplementary operations; working in a forced draught, use of additional reagents, etc.

EXPERIMENTAL

a) Quantitative Determination of Chlorine

Before starting an analysis, a stream of oxygen at a rate of 150–200 ml/minute is passed for 15–20 minutes through the apparatus assembled as shown in the diagram, the electric ovens being switched on. The first oven is



heated to 700°; the second to 800–900°. The oxygen stream is switched off at the end of this period. A moist tube C is inserted into a box containing porous potassium iodide, so that 3–4 g (equivalent to a layer of 80–100 mm) is freely picked up. In order to economize on potassium iodide, C need only be half filled. In this case, however, it is necessary to fix an additional tube c (not shown in the diagram) filled with potassium iodide or bromide, or sodium iodide or bromide, equivalent to a layer of 80–100 mm for a tube of diameter of 8–10 mm, between tube C and combustion tube a. If tube c is used it should be heated to 120–150° during the analysis, in order to trap small amounts of condensing aqueous solutions of hydrogen halides and free halogens. Absorbent tube e contains 8–10 ml of 10% potassium iodide.

An aliquot of test material in a porcelain boat is strewn with quartz sand and placed in the combustion tube at a distance of 3–4 cm from the first oven. Oven 1 is carefully moved onto the boat. The vapors of the material are carried into the calcining zone of the oven with the oxygen, where it is completely decomposed. Volatile, rapidly-evaporating materials must be ignited more carefully. When combustion is complete, oven 1 is moved next to oven 2. Most of the halogens and hydrogen halides are trapped in tube C filled with potassium iodide. The contents of tube C and the absorbent apparatus are quantitatively transferred to a flask; 10–20 ml of 0.05 N potassium biiodate is added and the iodine liberated titrated with 0.05 N sodium thiosulfate. The chlorine content is calculated from the formula:

$$\% \text{ Cl} = \frac{\text{Cl}(K_1 - K_2) \cdot 100}{20{,}000 \cdot a}$$

where Cl is the gram-equivalent of chlorine, K_1 – the number of mls of 0.05 N sodium thiosulfate used, K_2 – the number of mls of 0.05 N biiodate added, a – weight of sample.

b) Quantitative Determination of Bromine

Analysis is carried out as described above, but without addition of biiodate. Calculation of the bromine content is carried out by means of the formula:

$$\% \text{ Halogen} = \frac{\text{Halogen} \cdot K \cdot 100}{20{,}000 \cdot a}.$$

c) Quantitative Determination of Iodine

Analysis is carried out as for bromine, but in this case, tube c containing bromides and chlorides should not be inserted. The percentage of iodine is calculated by means of the same formula.

As a result of the decomposition of chlorine-containing materials, free halogens and hydrogen halides are formed which liberate an equivalent amount of iodine and hydrogen iodide from the moist potassium iodide; these can be titrated with sodium thiosulfate and alkali, or by the biiodate method, which is far simpler.

The percentage of chlorine in these cases is calculated by means of the formulas:

$$\% \text{ Halogen} = \frac{\text{Halogen} \cdot (K_1 + K_2) \cdot 100}{20{,}000 \cdot a};$$

$$\% \text{ Halogen} = \frac{\text{Halogen} \cdot (K_1 - K_3) \cdot 100}{20{,}000 \cdot a};$$

where Halogen is the gram-equivalent of the halogen determined; K_1 – the number of mls of 0.05 N sodium thiosulfate; K_2 – the number of mls of 0.05 N alkali; K_3 – the number of mls of 0.05 N biiodate; and a – the weight of sample.

As can be seen from the results given in the table below, quantitative determination of halogens carried out by two titration methods gives equally good results. Determination of halogens by the method of double titration may be useful in those cases where it is essential to know how much free halogens and hydrogen halides are formed during decomposition.

E. g. our experimental results indicate that during analysis of organic materials, even chlorine-containing organic materials which do not contain hydrogen (hexachlorcethane), always form some hydrogen chloride, apparently as a result of the partial formation of phosgene inside the combustion tube and subsequent hydrolysis with water

$$COCl_2 + H_2O \rightarrow 2HCl + CO_2.$$

Sample designation	Weight of sample in g	Volume in ml of 0.05 N solution used of		Number of mls of 0.05 N	% Halogen		
		$Na_2S_2O_3$	NaOH	$KH(IO_3)_2$	Calculated	Found	Difference
Dichlorobenzene	0.0648	4.16	13.50	–	48.23	48.37	+ 0.14
Hexachloroethane	0.0630	24.96	7.04	–	89.89	90.04	+ 0.15
Trichlorobenzene	0.0472	6.00	9.60	–	58.62	58.59	– 0.03
Tetrachlorophthalic acid	0.0492	4.14	8.80	–	46.66	46.62	– 0.04
Chloro-4-methyl 1-2-phenoxyacetic acid	0.0333	0.30	3.00	–	17.67	17.56	– 0.11
Bromocamphor	0.0341	2.96	–	–	34.57	34.68	+ 0.11
Tetrabromo-orthoxylene	0.0594	11.28	–	–	75.81	75.88	+ 0.07
Iodoform	0.0604	9.20	–	–	96.69	96.66	– 0.03
Dichlorobenzene	0.0528	35.44	–	21.10	48.23	48.15	– 0.08
Tetrabromo-ortho-xylene	0.0560	31.74	–	21.10	75.81	75.92	+ 0.11
Hexachloroethane	0.0270	34.78	–	21.10	89.89	89.82	– 0.07

Bromine and iodine, the less active halogens, do not form hydrogen halides. The hydrogen halides of these halogens are oxidized more easily than hydrogen chloride.

To check on the method we analyzed materials which are difficult to analyze. In all cases good results were obtained. Errors did not exceed ±0.1–0.2%. An analysis takes 55-60 minutes, which is twice as fast as the method involving combustion with a catalyst and iodometric titration.

SUMMARY

1. A new method has been worked out for the quantitative determination of chlorine, bromine, and iodine in organic materials.

2. The method is based on combustion of halogen containing organic compounds by heating in a rapid stream of oxygen without using catalysts.

3. In order to break up the cloud formed as the result of interaction of free halogens and hydrogen halides with water vapor, a filter tube is suggested. The tube is filled with fine crystalline material., e.g., chlorides, bromides, iodides.

4. The method is simple, reliable, rapid, and accurate enough. It does not require scarce and expensive reagents and apparatus.

The method can be universally applied and can be recommended for use in scientific-research, industrial, and educational laboratories.

Received April 25. 1954

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* T. p. = C. B. Translation pagination.

COPRECIPITATION OF CESIUM WITH POTASSIUM PICRATE

I. M. Korenman, P. A. Ganichev, and V. V. Gorshkov

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Precipitation of potassium as the picrate is used fairly often in qualitative and quantitative analysis [1-6]. In order to lower the solubility of potassium picrate, the reaction is carried out in the presence of alcohol and, as a consequence, the reagent used is an alcoholic solution of picric acid. It is known that the reagent precipitates rubidium, cesium, thallium and other cations in addition to potassium.

The aim of our work was to study coprecipitation of cesium on precipitation of potassium with an alcoholic solution of picric acid.

We used the radioactive isotope Cs^{134}_{55} for our studies. The preparation we used had an initial specific activity of 75 impulses/minute per γ of cesium. We started with 20 γ cesium and 2000 γ of potassium in 1 ml of aqueous-alcohol solution. The amount of the micro-component does not, on its own, give a precipitate with the reagent, while the macro-component gives a precipitate with a volume which it is convenient to handle. Precipitation was carried out as follows: into a series of centrifuge tubes were placed 0.6 ml of solution containing 2000 γ potassium and 20 γ cesium as the nitrates. These were mixed with 0.4 ml of 96% ethyl alcohol, and 0.5 ml of a 6% alcoholic solution of picric acid added. After mixing for one minute, the precipitate was centrifuged and the supernatant liquor sucked off with a pipet. Considerable difficulty was encountered in deciding on a wash liquor. The precipitate of potassium picrate dissolves fairly readily in water, ethyl alcohol, and other organic solvents, so that these liquids cannot be used for washing the precipitate. On the basis of a number of tests, we finally decided on secondary butyl alcohol as wash liquor, since the solubility of the precipitate in this solvent is comparatively low. After removal of mother liquor from the precipitate, the latter was washed three times (1 ml each time), with secondary butyl alcohol. The amount of coprecipitated cesium was determined on the washed precipitate radiometrically.

The tables below contain the average results of several determinations which agree quite well in each case. Even the first tests showed that appreciable amounts of cesium are precipitatedwith potassium picrate. We studied the influence of various factors on the coprecipitation of cesium. First we studied the effect of temperature on coprecipitation of cesium, for constant amounts of the macro- and micro- components. Precipitation was carriedout as described above, but with one difference; both test liquid and reagent were kept at a definite temperature for several minutes before mixing. Reckoning that a decrease in percentage coprecipitation might result at elevated temperatures as a result of increased solubility of precipitate, we weighed it and then calculated the amount of cesium coprecipitated with 1 mg of potassium. We were able to carry out tests at temperatures not exceeding 35°; at higher temperatures no precipitate was formed. Results of these determinations are given in Table 1.

The results obtained show that the use of alcoholic solutions of picric acid does not ensure against loss of precipitate because of its solubility. The best results for micro-determination of potassium are observed if precipitation is carried out at low temperatures. At 0° comparatively little potassium picrate remains in solution. The amount of cesium picrate coprecipitated is relatively small, and does not compensate for the loss which results from the solubility of the precipitate. Coprecipitation of cesium should not, therefore, affect the accuracy of potassium determinations. Coprecipitation may, however, lead to appreciable loss when it comes to subsequent determination of small amounts of cesium.

As will be shown below, coprecipitation of cesium with potassium picrate is isomorphous in character. We accordingly calculated Khlopin's constant [7], by means of the formula

$$\frac{x}{a-x} = D\frac{y}{b-y}$$

TABLE 1

Coprecipitation of cesium with potassium at various temperatures
(20 γ cesium and 2000 γ potassium in the test; theoretical weight of precipitate 13.7 mg)

Temperature, in °C	Weight of precipitate, in mg	Cesium coprecipitated			D
		in γ	in γ / mg precipitate	in %	
0	13.5	8.0	0.60	40.0	$9.8 \cdot 10^{-3}$
10	13.4	4.9	0.36	24.5	$7.2 \cdot 10^{-3}$
16	12.1	2.9	0.24	14.5	$2.2 \cdot 10^{-2}$
20	11.5	2.2	0.19	11.0	$2.3 \cdot 10^{-2}$
35	8.9	0.9	0.10	4.5	$2.5 \cdot 10^{-2}$

where: a is the initial concentration of the micro-component; b – the initial concentration of the macro-component; x – the amount of coprecipitated micro-component; y – the amount of precipitated macro-component; D – Khlopin's constant.

In our calculations we took into account not the amount of potassium, but the theoretical and experimentally determined weights of precipitate. This simplifies calculation, and gives the same results.

Khlopin's constant is calculated as follows, e.g., weight of precipitate 12.1 mg, theoretical weight of precipitate = 13.7 mg; initial amount of cesium 20 γ; amount of cesium coprecipitated 2.9 γ; consequently:

$$\frac{2.9}{30-2.9} = D\frac{12.1}{13.7-12.1}$$

from which $D = 2.2 \cdot 10^{-2}$.

Khlopin's constant, as is evident from Table 1 is less than 1. Consequently, during precipitation, the crystalline phase becomes poorer in the micro-component as compared with the amount of it which remains in the mother liquor.

If in the original solution the ratio of the amount of cesium to potassium is equal to 1 : 100, then in the precipitate we get, at 0°, a ratio of 1 : 1660, and at 35° the ratio becomes 1 : 10,000. In spite of this, however, it is possible to separate up to 40% of cesium at 0°. In addition, we see that changes in temperature lead to changes in Khlopin's constant, which can be explained by various changes in the solubilities of the picrates of potassium and cesium with temperature. Since changes in temperature affect the solubility of the precipitate, we carried out subsequent experiments at a constant temperature of 16°. Next, we studied the effect of length of time for which the precipitate is allowed to stand in contact with mother liquor on cesium coprecipitation. Tests were carried out with constant amounts of cesium and potassium, in which precipitation conditions were also kept constant. The precipitates were centrifuged after various time intervals from the addition of reagent. In freshly precipitated potassium picrate we found 14.5% of the cesium taken, while in precipitates allowed to stand in contact with the mother liquor for 72 hours, we found 13.6% cesium.

Consequently, the time of standing of precipitate in mother liquor has no appreciable effect on the amount of cesium coprecipitated. In further tests, therefore, it was immaterial whether tests were carried out on the precipitate immediately after precipitation, or after standing.

We also investigated the effect of protective colloids on cesium coprecipitation; for this purpose we introduced starch, agar-agar, and gelatin, respectively, in such amounts that the total volume of solution (1.5 ml) remained constant (Table 2) to the original solution. In each case 0.4 ml of a 0.01% solution of protective colloid was added.

Protective colloids depress the amount of cesium coprecipitated very little, on an average ca. 1%.

In another series of tests, the same amount of cesium was added to potassium picrate already precipitated. The amount of cesium was determined after being shaken up with this precipitate for 10 minutes. In all cases this amounted to ca. 2-3%. These observations indicate that coprecipitation is isomorphous in character.

Leaving the experimental conditions unchanged, we studied the effect of the amount of the micro-component on the amount of it coprecipitated, for a constant amount of macro-component. 2000 γ of potassium was used. This amount should, theoretically, give 13.7 mg picrate; nevertheless, at 16° the amount of precipitate found was only 12.1 mg. These results were taken into account in calculating Khlopin's constant (Table 3).

TABLE 2

Coprecipitation of cesium with potassium picrate in the presence of protective colloids (20 γ cesium and 2000 γ potassium in the test)

Additive	Cesium coprecipitated in %
None	14.5
Gelatin	13.4
Agar-agar	13.2
Starch	13.6

TABLE 3

Coprecipitation of cesium with potassium picrate when the amount of the micro-component is varied

Cesium content in γ	Ratio of $Cs^+:K^+$ before precipitation	Cesium coprecipitated		D
		in γ	in %	
25	1:80	4.0	16.0	$2.5 \cdot 10^{-2}$
20	1:100	2.8	14.0	$2.1 \cdot 10^{-2}$
15	1:133	2.3	15.3	$2.4 \cdot 10^{-2}$
10	1:200	1.6	16.0	$2.5 \cdot 10^{-2}$
5	1:400	0.8	16.0	$2.5 \cdot 10^{-2}$

It is clear from Table 3 that with decreasing amount of the micro-component, the average percentage cesium coprecipitated remains constant. The Khlopin constant, within the limits of experimental error, remains practically constant [$D = (2.4 + 0.1)\,10^{-2}$], which is a very convincing argument for the isomorphous character of the coprecipitation of cesium with potassium picrate. These results testify to a rapid achievement of thermodynamic equilibrium.

Next, we varied the amount of macro-component, while leaving the amount of micro-component unchanged, as well as the precipitation conditions, in particular, keeping constant the amount of added reagent and the final volumes (Table 4).

TABLE 4

Coprecipitation of cesium with potassium picrate on varying the amount of the macro-component (20 γ cesium in the test)

Amount of potassium in γ	Ratio of $Cs^+:K^+$ before precipitation	Weight of precipitate in mg	Cesium coprecipitated			D
			in γ	γ / mg precipitate	in %	
1500	1:75	8.8	2.3	0.26	11.5	$2.2 \cdot 10^{-2}$
2000	1:100	12.1	2.9	0.24	14.5	$2.2 \cdot 10^{-2}$
2500	1:125	14.8	3.9	0.26	19.5	$3.8 \cdot 10^{-2}$
3000	1:150	17.8	4.1	0.23	20.5	$3.9 \cdot 10^{-2}$
4000	1:200	21.5	4.3	0.20	21.5	$7.5 \cdot 10^{-2}$

It follows from the results given in Table 4 that the amount of the micro-component coprecipitated with 1 mg of precipitate remains practically constant with changes in the amount of macro-component, but the percentage coprecipitation of cesium increases with increasing amounts of macro-component, and Khlopin's constant increases. With changes in the amount of the macro-component, the precipitation conditions are, of course, different and this leads to changes in the value of D.

SUMMARY

1. It has been established that, on precipitating potassium with an alcoholic solution of picric acid, cesium is coprecipitated in appreciable amounts.

2. A number of factors which influence coprecipitation of cesium have been studied, and it has been found that the appearance of cesium in the potassium picrate is the result of isomorphous precipitation.

3. Coprecipitation of cesium does not affect the accuracy of potassium determinations, but leads to essential losses in subsequent determinations of small amounts of cesium.

4. It has been shown that the use of an alcoholic solution of picric acid gives satisfactory results for the quantitative determination of potassium only when precipitation is carried out at 0°.

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BRIEF COMMUNICATIONS

A DESIGN FOR AN A.C. ARC WITH MAGNETIC STABILIZATION FOR SPECTRAL ANALYSIS

P. F. Lokhov

Papers have been published [1, 2], on the question of obtaining an A.C. arc discharge with impulse characteristics, and with a definite scattering of the impulses along the surface areas of the electrodes, in which factors relating to the stabilization of the arc spectra in the case of ferromagnetic electrodes were put forward.

The present article contains a brief description of a new electrical set-up, which permits one to treat the discharge surface of copper electrodes uniformly with an electric discharge. This permits a significant increase in accuracy and sensitivity in the analysis of solutions placed as drops on flat copper electrodes and allowed to dry out. This set-up also permits stabilization of the intensity of the spectra between ferromagnetic electrodes by a simple method.

The Electrical Set-up

The electrical set-up for an A.C.-arc with magnetic stabilization (Fig. 1) differs from the Sventitsky activated A.C. arc [3], in that an additional active resistance R_2 is included in the circuit as well as four spark gaps (instead of one) in the discharger of the oscillating circuit and a self-induction coil L_3.

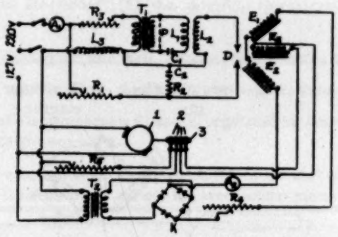

Fig. 1. Set-up for an A.C. arc with magnetic stabilization: A_1—A.C. ammeter; R_1—arc rheostat; R_2—non-wire (non-linear) resistance of type BC; C_2—blocking condenser; R_3—rheostat for transformer T_1; L_3—self induction coil; P—discharger with 4 spark gaps; C_1—oscillating circuit condenser; L_1, L_2—primary and secondary windings of H.F. transformer; D—arc gap; E_1, E_2—D.C. electromagnet; E_3—A.C. electromagnet; T_2—transformer for copper oxide rectifier, K; A_2—D.C. ammeter; R_4—rheostat for D.C. electromagnets; R_5—rheostat for A.C. electromagnet; 1, 2, 3—motor, brushes, and rotor for the synchronous throw-over switch.

The non-linear resistance R_2 of type BC is introduced so that no spark discharge conditions come into operation in the generator at low current strength, and to ensure stable arc burning. For this purpose, rheostat R_2 of the set-up described before was used [1, 2].

The scientific technical basis for the use of a resistance to ensure operation of the generator at low current strengths is given in Abramson's paper [4], where it is recommended that the resistance be connected in parallel and not in series to the blocking condenser. In the given set-up, however, resistance R_2 is connected in series, since the method of connecting in series has been in use for many years in a large number of laboratories (since 1942).

The additional spark gaps in the discharger have been introduced in order to increase spectra stability. Two spark gaps were used for this purpose in the previous work [1, 2].

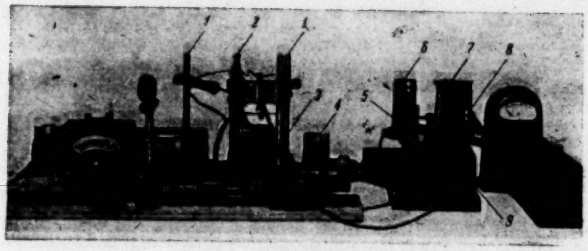

Fig. 2. A.C. arc generator with magnetic stabilization: 1) D.C. electromagnets; 2) A.C electromagnets; 3) copper oxide rectifier, type BAK-10; 4) synchronous throw-over switch; 5) discharger with spark gaps; 6) self-induction coil L_3; 7) H.F. transformer; 8) oscillating circuit condenser, type KOS-13, total capacity 2500 $\mu\mu$F, and 8000 V; 9) non-linear resistance R_2 of 102 Ω; 10) VT (five VS-type resistances, 510 Ω each, in parallel).

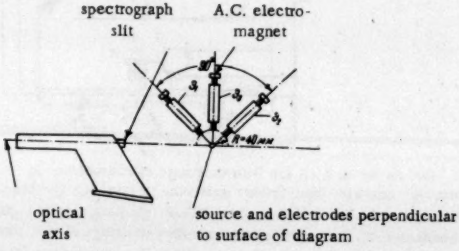

Fig. 3. Arrangement of the electromagnets.

The self induction coil L_3 is used as a more reliable method of protecting the circuit from penetration by H.F. currents. The inductive resistance of the coil is equal to the inductive resistance of the secondary winding of the H.F. transformer.

The difference between the action of an arc with magnetic stabilization and the usual type is that D.C. and A.C. magnetic fields are superimposed on the usual activated arc discharge, as a result of which the discharge surface of the electrode sparks uniformly; consequently, test material passes more uniformly into the excitation zone of the atomic spectra.

Electromagnets E_1 and E_2 are supplied with D.C. via a copper oxide rectifier. The electrical circuit for supplying the electromagnets consists of a step-down transformer T_2, a copper oxide rectifier K, rheostat R_4 and ammeter A_2. Electromagnet E_3 is supplied with A.C. through a synchronous throw-over switch and rheostat R_5.

The synchronous throw-over switch consists of a synchronous SD = 60 motor, brushes 2, rotor 3, and is designed to change the direction of the current flowing through the arc. The rotor and brushes permit contact to be made and broken with the contacts to the windings of the electromagnet E_3 four times a second. Using a set-up of this type it is possible to get a band of arc impulses, perpendicular to the optical axis of the spectrograph, by means of the electromagnets E_1 and E_2. This band is deflected by electromagnet E_3, first to one side and then to the other half of the discharge surface of the electrodes which determines uniform treatment of it by the electric discharge. A general view of the generator is shown in Fig. 2. In order to get an arc discharge with distribution of the impulses along all the surface of the operating areas between ferromagnetic electrodes, it is sufficient to fix up one of the D.C. electromagnets proposed in the scheme set out above a little higher than the source, and another one slightly lower than the source, to magnetize the electrodes at a distance. The distance of the electromagnets from the source and their arrangement in the plane remains unchanged (Fig. 3).

Suggested Values for the Operating Parameters and Rules for the Use of the Apparatus

On the basis of experience in operating an A.C. arc with magnetic stabilization for spectrochemical analysis on copper electrodes (this term is given to the method by analogy with the term used in the literature: "Spectrochemical Analysis with Spark Excitation on Copper Electrodes") [5], the following approximate operating parameters can be recommended.

1. The arrangement of the electromagnets and their distances to the source should be the same as in Fig. 3.

2. The current in the circuit of transformer T_1 regulated by rheostat R_3 should be 0.5 A.

3. The currents in the circuits of electromagnets E_1 and E_2 regulated by rheostat R_4, and measured by ammeter A_2, should be 0.3 A; each magnet has 2500 turns.

4. The current in the circuit of electromagnet E_3 should be 0.1 A; the electromagnet has 5000 turns. To measure the current in the electromagnet E_3 it is necessary to cut out the synchronous motor and to turn the rotor so that the circuit of electromagnet E_3 is closed.

Control over the sparking of the electrode discharge surfaces is possible by visual observation through a blue glass (protected from the ultraviolet).

Received October 12, 1954

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A NEW QUANTITATIVE METHOD OF DETERMINING ARSENIC AS THE PENTASULFIDE

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The sulfide methods are described in the literature for the quantitative determination of arsenic. In one of these methods arsenic is determined As_2S_3 after precipitation with hydrogen sulfide. This method requires that arsenic should be in the trivalent state and gives good results.

In the other method, arsenic is weighed as As_2S_5 after precipitation with hydrogen sulfide from a cold, strong hydrochloric acid solution. In this case the quinquevalent arsenic is partly reduced to the trivalent state. The precipitate of As_2S_5 obtained invariably contains As_2S_3 and free sulfur. The composition of the precipitate depends on precipitation conditions, solution concentration, temperature, etc.

It is still possible, however, to get accurate results for the gravimetric determination of arsenic as As_2S_5 if certain conditions are observed. Quinquevalent arsenic is precipitated under normal conditions with hydrogen sulfide. The precipitate thus obtained is dissolved in ammonium polysulfides, and the solution acidified with dilute hydrochloric acid. The precipitate containing As_2S_3 and S, is filtered off, washed with CS_2 to remove sulfur, dried and weighed as As_2S_5.

TABLE 1

As taken in g	As found by means of the new sulfide method	Error in %
0.00434	0.0046	+ 0.0003
0.0217	0.0219	+ 0.0002
0.0434	0.0430	− 0.0004
0.0434	0.0434	± 0.0000

TABLE 2

As found in g		
New sulfide method	Method of Bunsen and Neer	In the form of $Mg_2As_2O_7$
0.0732	−	0.0734
0.0737	−	0.0735
0.0735	−	0.0734
0.1057	0.1054	−
0.1058	0.1058	−
0.1054	0.1055	−

Test solution containing 0.1 g of arsenic is introduced into a 200 ml conical flask, and strongly acidified with concentrated HCl (1 part solution 2 parts concentrated HCl); hydrogen sulfide is then passed through it. When the solution is saturated with hydrogen sulfide, the flask is stoppered and allowed to stand for several hours, being given an occasional shake.

The precipitate is filtered through an ordinary filter and washed with distilled water to remove HCl. The filter and precipitate are transferred to the flask in which the arsenic was originally precipitated and worked up with small amounts of freshly prepared, colorless, or pale yellow ammonium sulfide. Excess ammonium sulfide must be avoided.

The ammonium sulfide combines with free sulfur to form polysulfides which oxidize trivalent arsenic. The filter is then washed with distilled water. The filtrate is acidified with dilute HCl, when As_2S_5 and S are precipitated.

Solution + precipitate are heated on a boiling water bath and the whole stirred periodically until the liquid becomes completely clear (ca. 1/2 hour); after cooling, the precipitate is filtered through a Scott1-G crucible, washed with distilled water, absolute alcohol, and carbon disulfide, which is added in small amounts till all the sulfur is removed. The precipitate is finally dried at 105° to constant weight.

Results of arsenic determinations are given in Tables 1 and 2.

Received October 10, 1954

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CHRONICLE

ANATOLI KONSTANTINOVICH RUSANOV

(On his fiftieth birthday)

The All-Union Scientific Research Institute of Mineral Raw Materials, the State Institute of Rare and Precious Metals, the All-Union Scientific Research Institute of Hydrogeology and Engineering Geology, the Commission on Spectroscopy of the USSR Academy of Sciences, and a number of other organizations, warmly note the 50th birthday of Anatoli Konstantinovich Rusanov, a professor and a Doctor of Technical Sciences, who is one of our foremost specialists in spectral analysis of ores, minerals, and rocks.

The Ministry of Geology and Preservation of the Resources of the USSR has observed the 50th birthday of Rusanov by awarding him the Order of Socialist Competition.

A. K. Rusanov was born on May 1, 1905, in Moscow to the family of an office worker. He received his advanced education in the Chemical Section - Physical Mathematical Faculty of Moscow University; he went to lectures and worked in the laboratories of I. A. Kablukov, N. D. Zelinsky and other famous scientists.

He started working at 15 in the library of the Committee of State Defense (1920-1923).

In 1929 he entered the All-Union Institute of Mineral Raw Materials, where he started to organize a laboratory for spectral analysis and managed in a fairly short time to demonstrate the great possibilities of this method for studying the quality and properties of useful minerals. He became a specialist in spectral analysis of ores and minerals.

Behind this success was A. K. Rusanov's creative initiative in posing scientific theoretical problems and his capacity to utilize their results for developing new methods for the qualitative and quantitative spectral analysis of ores, minerals, and rocks. He studied complex phenomena on carbon electrodes during spectral analysis of ores, and established general rules for measuring line spectra intensity in relation to ore composition. He also compiled a volatility series for the elements by means of which it is possible to forecast the order in which elements pass into the arc and also established general rules for the successive changes in temperature conditions of spectra excitation during evaporation of the ores.

On the basis of his theoretical studies, Rusanov proposed new methods for spectral determination of rare and scattered elements in ores; cadmium, lithium, germanium, hafnium, etc.

In his work, A. K. Rusanov relied on a complex method of studying mineral raw materials and in the course of his long activity has maintained a close connection with chemists, geochemists, mineralogists, geologists, and technologists.

Apart from theoretical and methodological work, Rusanov has paid considerable attention to the apparatus used in spectral analysis; he has constructed a number of gadgets for quantitative spectral analysis. He has developed and introduced into practice spectrally pure carbon.

He has played an important part in training cadres and organizing a network of spectral laboratories in geological organizations which has had a great effect on increasing the tempo and efficiency of geological prospecting. He has participated in many conferences and exchanged his ideas with others.

He has published over 50 papers. Among his published work, of great scientific and practical importance is his work on "The Spectral Analysis of Ores and Minerals". This book has been translated into Polish and Chinese.

Rusanov has also organized a spectral laboratory for "Giredmet", the workers in which have carried out much work on rapid methods of control of technical processes for obtaining rare metals, and also introducing these methods into practice. He has also given help in organizing a laboratory within VSEGINGEO.

In addition to his scientific work Rusanov was a teacher in the I. V. Stalin Moscow Mining Institute from 1930-1940.

In 1947 he successfully defended his thesis for his doctorate of technical sciences and in 1952 he was given the title of professor. Under his guidance a number of his coworkers have also defended their theses for degrees.

Rusanov participates a lot in social activity. For 10 years he has been a member of the Commission of Spectroscopy of the USSR Academy of Sciences, of the Scientific Committee of VIMS and Giredmet, heading the sections on spectral analysis of ores and minerals. In 1953 he was chosen as a member of the Commission of Analytical Chemistry of the USSR Academy of Sciences. Starting in 1950, Rusanov has been elected three times as a deputy to the Moscow Soviet, and has carried out his duties on behalf of his electors. He also participated actively in the work of the Moscow Soviet Commission for improving the city, and heads a brigade for improving boulevards and squares.

He is also a member of the Moscow Committee of the Trade Union for Geological and Prospecting Workers.

He has been rewarded by the Government for his scientific work with the Order of the Red Banner, Order of Honor, and three medals. He has been outstanding in socialist competition in the Construction Materials and Non-Ferrous Industries.

We wish Rusanov many more years of creative work in the service of our great country.

I. V. Shmanenkov

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